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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1537

Part of Journal of Research of the National Bureau of Standards, Volume 30, May 1943

DISSOCIATION CONSTANTS AND pH-TITRATION CURVES AT CONSTANT IONIC STRENGTH FROM ELECTROMETRIC TITRATIONS IN CELLS WITHOUT LIQUID JUNCTION: TITRATIONS OF FORMIC ACID AND ACETIC ACID

By Roger G. Bates, Gerda L. Siegel, and S. F. Acree

ABSTRACT

An improved method for obtaining the titration curves of monobasic acids is outlined. The sample, 0.005 mole of the sodium salt of the weak acid, is dissolved in 100 ml of a 0.05-*m* solution of sodium chloride and titrated electrometrically with an acid-salt mixture in a hydrogen–silver-chloride cell without liquid junction. The acid-salt mixture has the composition: nitric acid, 0.1 *m;* potassium nitrate, 0.05 *m;* sodium chloride, 0.05 *m*. The titration therefore is performed in a medium of constant chloride concentration and of practically unchanging ionic strength (μ=0.1). The calculations of pH values and of dissociation constants from the emf values are outlined. The titration curves and dissociation constants of formic acid and of acetic acid at 25° C were obtained by this method. The p*K* values (negative logarithms of the dissociation constants) were found to be 3.742 and 4.754, respectively.

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I. INTRODUCTION

It has long been recognized that measurement of the changes of pH during the neutralization of a weak acid with alkali can be employed to obtain an accurate value for the strength of the acid or its dissociation constant. In electrometric titration, the pH values are measured at successive steps in the titration by means of the changing potentials of suitable electrodes immersed in the solution. According to usual practice, successive portions of a solution of strong alkali are added to a sample of pure acid, and the pH values of the several mixtures are determined. The titration is performed in a cell that contains a hydrogen, glass, or quinhydrone electrode. The cell

system is completed by a reference half-cell (calomel, silver chloride, etc.) whose electrolyte is brought into liquid-liquid contact with the acid solution in the titration vessel.

The pH values that are derived from the emf measurements of such a cell often involve considerable uncertainty, and in unfavorable cases they may be in error by more than 0.05 pH unit [1, 2].[1] The principal reason for this difficulty is neglect of the contribution of the potential at the liquid junction or in the application of improper or inadequate corrections for it. Such corrections are laborious and unsatisfactory and require a knowledge, often unavailable, of the mobilities and activities of the ions of which the solutions are composed. For accurate work, liquid junctions are to be avoided whenever possible. For approximate work, however, cells with a liquid junction are often useful.

The second limitation to the accuracy of these titrations has its origin in the changing concentration of ionized solutes in the cell during the titration. A solution of the weak acid has a low ionic strength, whereas its salt is a strong electrolyte. It is well known that there is an infinity of titration curves for a particular weak acid, each one corresponding to a different ionic strength. Although the effect of the change in ionic strength on the pH values measured during the course of the titration may be small, the titration curve will be distorted unless the total ionic concentration is held at a constant value while the series of experiments is being performed. As a rapid means of obtaining dissociation constants of weak electrolytes, however, the titration procedure has much to recommend it. It has seemed worth-while, therefore, to attempt to improve its accuracy.

It is the purpose of this paper to present a method for obtaining pH-titration data and dissociation constants for weak monobasic acids by means of electrometric titrations in a hydrogen–silver-chloride cell without liquid junction. An alkali-metal salt of the weak acid in sodium chloride solution is titrated with nitric acid solution to which have been added sodium chloride and potassium nitrate in amounts sufficient to maintain unchanging chloride concentration and constant ionic strength as the salt is changed into weak acid. The method has been applied to the determination of the dissociation constants of formic acid and of acetic acid. Comparison with the best data in the literature indicates that pK values accurate to 0.01 unit were obtained.

II. DISCUSSION OF THE TITRATION METHOD

When an electrometric titration is performed, data for the entire titration curve are ordinarily obtained within 3 or 4 hours. Unusual precautions must therefore be exercised to insure rapidity of equilibrium after the addition of each increment of acid or alkali. The potential of the hydrogen electrode adjusts itself rapidly, in the absence of oxygen, to changing pH. The silver chloride electrode, however, is slow to come to equilibrium when the chloride-ion concentration is changed, for equalization of the chloride-ion concentration in the porous electrode and in the solution must take place by

[1] Figures in brackets indicate the literature references at the end of this paper.

diffusion. When constant chloride-ion concentration is maintained, however, equilibrium is rapid, and the emf values may be obtained readily. The calculation of pH values and of the dissociation constant of the weak acid from the experimental data are described in detail in the following sections.

1. TITRATION CURVES AT CONSTANT IONIC STRENGTH FROM CELLS WITHOUT LIQUID JUNCTION

The hydrogen–silver-chloride cell without liquid junction may be represented by the following arrangement:

$$\mathrm{Pt|H_2|H^+,\ Cl^-|AgCl|Ag}, \tag{1}$$

where H^+ and Cl^- represent the components of the cell electrolyte to which the cell is reversible. The emf of the cell at a centigrade temperature, t, is related to its standard potential, $E°$, and to the activities, $\boldsymbol{a}$, of these two ions by the equation

$$\frac{(E-E°)\boldsymbol{F}}{2.3026RT} = -\log(\boldsymbol{a}_{\mathrm{H}}\boldsymbol{a}_{\mathrm{Cl}}) = (E-E°)/k, \tag{2'}$$

or

$$-\log \boldsymbol{a}_{\mathrm{H}} = (E-E°)/k + \log \boldsymbol{a}_{\mathrm{Cl}}, \tag{2}$$

where R is the gas constant (8.3127 Int. j. $\mathrm{deg^{-1}\ mole^{-1}}$ [3]), T is the absolute temperature (t+273.16) [4], $\boldsymbol{F}$ is the faraday (96,500 Int. coulombs [4]), and k is written for 2.3026 $RT/\boldsymbol{F}$.

The problem of determining pH ($=-\log \boldsymbol{a}_{\mathrm{H}}$) from emf measurements of cells of type 1 resolves itself into estimation of the activity coefficient, f_i, of chloride ion. It is noteworthy that all methods of pH determination must deal with this theoretical difficulty in one form or another[2]. The least ambiguous solution is possibly that which assumes a simple relation among the activity coefficients of all the ions of which the mixture is composed. Thus the activity coefficient of chloride ion (and of other singly charged ions) is considered to be equal to the mean activity coefficient of hydrochloric acid in the mixture.

The activity coefficient of any ion species, i, in the mixture may be represented by the Hückel equation [5],

$$-\log f_i = \frac{Az_i^2\sqrt{\mu}}{1+Ba_i\sqrt{\mu}} - \beta\mu, \tag{3}$$

where μ is the ionic strength ($\frac{1}{2}\Sigma m_i z_i^2$), z_i is the valence of the ion, the molality of which is m_i, and A and B are constants that vary only with the temperature and dielectric constant of the solution. The values of A and B at 20°, 25°, and 30° C [6] are given in table 1, together with $E°$ and k.

When the proper values of parameters a_i and β are used, eq 3 describes the change of the activity coefficient of hydrochloric acid with ionic strength of the mixture. The parameter a_i has dimensions of length and is often called the "ion size." Only singly charged ions are involved in the titration of monobasic acids by the method outlined here. In this paper, therefore, f_i represents the activity coefficient of a univalent ion.

[2] A critical comparison of errors involved in determining pH from cells with liquid junction and from cells without liquid junction has been made by Hamer [2].

TABLE 1.—*Numerical values of $E°$, k, A, and B at 20°, 25°, and 30° C*

t	$E°$	k	A	B
°C	*Int. v*	*Int. v*		
20	0.22550	0.05815	0.505	0.329
25	.22238	.05914	.510	.330
30	.21911	.06013	.515	.331

Since $a_{Cl}=f_{Cl}m_{Cl}$, where m represents molality, eq 2 and 3 can be combined, as shown by Hamer and Acree [7], to give an expression which can be used for the computation of pH values from emf measusements. The term $\beta\mu$ in eq 3 is a secondary correction to the pH at low ionic strengths[3] but is very important at high concentrations. It is usually found to contribute less than 0.01 unit to the pH value at an ionic strength of 0.1. For approximate pH determination, $\beta\mu$ may safely be neglected. When both m_{Cl} and μ are the same for a series of emf measurements, eq 2 becomes simply

$$\mathrm{pH}=(E-E°')/k, \tag{4}$$

where $E°'$ is defined by

$$E°'=E°-k\log m_{Cl}-k\log f_i. \tag{5}$$

These conditions of constant chloride molality and of constant ionic strength over the entire range of the titration curve [4] were achieved by the proper choice of concentrations for the solution of the sodium salt to be titrated and for the components of the acid mixture with which the titration was performed. The sample, 0.005 mole of the sodium salt of the weak monobasic acid was dissolved in 100 ml of 0.05-m sodium chloride solution. The acid mixture was composed of nitric acid at a molality of approximately 0.1, together with potassium nitrate and sodium chloride, each at a molality of 0.05.

In two experiments, the sample was dissolved in 200 ml of 0.05-m sodium chloride solution. The ionic strength in these two titrations was therefore about 0.077 instead of 0.1 and changed about 6 percent during the titration. Another titrating solution which contained somewhat less potassium nitrate could have been used to offset this change in ionic strength.

2. DISSOCIATION CONSTANTS

The negative logarithm of the apparent dissociation constant of the acid, pK', at the ionic strength of the experimental solutions, is given by

$$\mathrm{p}K'=(E-E°)/k+\log m_{Cl}-\log (M_A/M_{HA}), \tag{6}$$

which, combined with eq 5, gives

$$\mathrm{p}K'=(E-E°')/k-\log (M_A/M_{HA})-\log f_i, \tag{7}$$

[3] If β has a value of 0.1, $\beta\mu$ is about 9 percent of $-\log f_i$ at an ionic strength of 0.1, and only 0.6 percent at an ionic strength of 0.001.

[4] The principle of constant anion or cation concentration in the titration of salts of weak acids or bases in cells with liquid junction was used by Meacham, Hopfield, and Acree [8] and by Mellon, Acree, Avery, and Slagle [9].

where M_A/M_{HA} represents the mole ratio of acid anion to undissociated acid. This ratio is obtained in the usual way by correcting for the dissociation of the weak acid. The correction for dissociation contributes only 4 percent (0.002 pH unit) to the ionic strength for the most acid formate mixture and accordingly need not cause serious concern in a determination of this type. Here again, a decrease in the amount of potassium nitrate used in the titrating acid would compensate for this small change in ionic strength.

Since the values of the activity coefficients of chloride ion and of the acid anion in the mixtures may not actually be identical (as assumed in eq 6), pK' differs somewhat from the negative logarithm of the true dissociation constant, pK[5]. The true pK can be obtained, however, from pK' values at two or more ionic strengths by extrapolation to the limit, $\mu=0$, where the two activity coefficients are both unity.

The change of apparent dissociation constant with ionic strength is small for most monobasic acids. For formic acid, pK' at an ionic strength of 0.1 is 0.009 unit higher than the value at zero concentration [10], whereas the measurements of Harned and Ehlers [11] indicate that the corresponding increase in pK' for acetic acid is even smaller, or about 0.005 unit. The observed difference between pK' at the two ionic strengths (0.1 and 0.077) used here should accordingly be about 0.002 unit, or less than the error of the measurement. An extrapolation was therefore not attempted.

The choice of a_i (eq 3) has no bearing upon the value of pK obtained, for f_1 does not influence the values of pK' derived from eq 6 and 7. The accuracy of the pH values (eq 4), however, is limited by the uncertainty in log f_i and, consequently, in $E^{\circ\prime}$.

Although there is no known means of predicting the numerical values of the constants of the Hückel equation for a particular mixture, it is probable that an a_i value between 3 and 5 A is required to represent the activity coefficient of hydrochloric acid in most solutions of uni-univalent salts.[6] As a mean value, therefore, 4 A has been chosen for the computation of the pH values. The contribution of the activity coefficient to the pH at an ionic strength of 0.1 is, then, assumed to be 0.114 unit. Had 3 A been used for a_i, the pH values would all have been lower by 0.009 unit, and the use of 5 A would have resulted in an increase of 0.008 unit over those values listed in tables 2 to 7. An accuracy of ± 0.01 unit can probably be ascribed to the pH values.

[5] As an alternate explanation of the slope of the plot of pK' with respect to μ, the activity coefficient of the undissociated acid, assumed to be unity in eq 6 and 7, can be considered to change, while the activity coefficients of chloride ion and of acid anion remain identical at all ionic strengths. Both assumptions lead to the same value of pK.

[6] Values of a_i between 3 and 5 A have also been found to be characteristic of mixtures which contain bivalent ions. A value of 3.8 A was found to give the best representation of the activity coefficient of hydrochloric acid in mixtures of primary phosphate, secondary phosphate, and sodium chloride at room temperature [12]. In sodium acid malonate-disodium malonate-sodium chloride buffers, 4.75 A gives the proper expression for the activity coefficient [6]. In unpublished measurements in this Bureau, W. J. Hamer has found the value of 3.76 A to apply both to mixtures of phthalic acid, potassium acid phthalate, and potassium chloride, and to mixtures of acid potassium phthalate, dipotassium phthalate, and potassium chloride. Unpublished work by the authors of this paper, however, showed that an a_i value of 8 A was required to represent correctly the activity coefficient function in buffers of potassium *p*-phenolsulfonate, sodium hydroxide, and sodium chloride. In a study of two completely dissociated mixtures of uniunivalent electrolytes, W. J. Hamer and G. D. Pinching (unpublished work) have found 3.5 A to apply to hydrochloric acid-potassium *p*-phenolsulfonate solutions and to solutions which contain hydrochloric acid and sodium 4-chlorophenol-2-sulfonate.

III. DISSOCIATION CONSTANTS OF FORMIC AND ACETIC ACIDS AT 25° C

1. MATERIALS

Sodium chloride and potassium nitrate that conformed with specifications of the American Chemical Society were recrystallized once before use. Sodium formate and sodium acetate of reagent grade were found to be sufficiently pure. Two samples of sodium formate were assayed by evaporating a mixture of the salt and sulfuric acid to dryness and weighing the residue. Both analyses gave 99.96 percent, calculated as sodium formate. Two samples of sodium acetate treated in the same way gave 99.89 percent and 99.92 percent. Three further analyses made by heating the salt with dilute sulfuric acid, distillation of the acetic acid, and titration with standard alkali, however, gave 100.27 ± 0.08 percent, calculated as sodium acetate. The presence of 0.1 percent of inert impurity in the sample of sodium salt results in an error of 0.001 unit in pK' at the midpoint of the titration; when the titration is 90 percent complete, the error in pK' is 0.004 unit.

All of the salts were powdered and dried at 110° C before use. The sodium acetate was partially dehydrated over concentrated sulfuric acid at reduced pressure before it was subjected to elevated temperatures.

The stock solution of sodium chloride was prepared from weighed amounts of water and of the dry salt. The acid solution was prepared by dissolving sufficient colorless concentrated nitric acid in water to make a solution approximately 0.1 *m*. Clean dry air had been bubbled through the nitric acid to remove oxides of nitrogen. The solution was weighed and a preliminary, rough determination of its acid content made. Enough sodium chloride and potassium nitrate were added to make the titrating solution 0.05 *m* with respect to each salt. Hydrogen was then passed through the solution to remove dissolved air. The acid solution was kept under hydrogen in storage flasks of Pyrex glass.

All rubber tubes or stoppers exposed to the nitric acid solution or vapor were coated lightly with paraffin, and the storage vessel was protected from light. Black paper that covers the flask or bottle completely is considered preferable to the use of a dark bottle for this purpose, since it facilitates inspection of the solution for the appearance of the yellow color which indicates decomposition of the nitric acid. If a yellow color should appear, hydrogen saturated with moisture should be bubbled through the solution for some time. The acid value should then be redetermined.

The acid titrating solution was standardized by weight titrations with a carbonate-free sodium hydroxide solution which, in turn, had been standardized against acid potassium phthalate, NBS Standard Sample 84a. The average deviation of the analyses was 0.03 percent.

The water thermostat, the potentiometric equipment, and the preparation of the hydrogen electrodes have been described in an earlier publication from this Bureau [12]. The silver–silver-chloride electrodes were of a semimicro type, designed to reduce the possibility of poisoning of the hydrogen electrodes by the deposition of silver upon the catalytic surfaces. Poisoning did not occur in any case.

Loops of platinum wire about 6 mm in length, sealed into soft glass, served as bases for the electrodes. A coating of silver, approximately 16 mg in weight, was formed on each loop by the thermal decomposition of silver oxide. The electrodes were chloridized in 1 *M* hydrochloric acid for 15 minutes with a current of 3 ma.

2. PROCEDURE

The titration cell is a modification of a cell for titrations with liquid junction previously described by Burton, Hamer, and Acree [13].

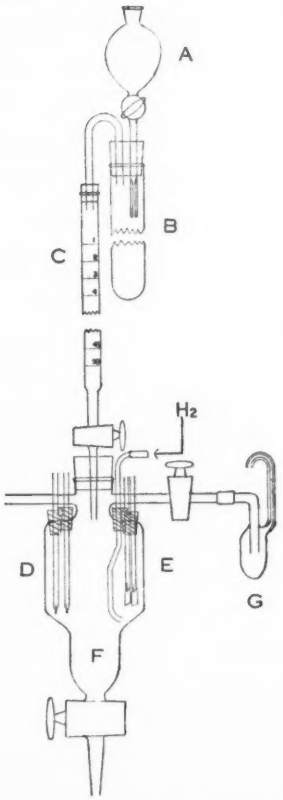

FIGURE 1.—*Assembly of apparatus for electrometric titrations without liquid junction.*

The arrangement of electrodes and burette in the cell is shown in figure 1.

The weighed sample of the sodium salt of the weak acid was introduced into the titration cell, *F*, and the sodium chloride solution was added from a calibrated pipette. The two platinized electrodes, *E*, were fixed in place by means of small rubber stoppers, and the hydrogen flow was started. The silver chloride electrodes, *D*, were usually placed in the cell just before the titration was begun—at the time when the burette was filled. Both the silver chloride electrodes and the hydrogen electrodes were usually freshly prepared for each series of experiments. The silver chloride electrodes were kept in

0.05-*m* sodium chloride solution until used, and the platinized foils were stored in distilled water.

The two silver chloride electrodes usually agreed in potential within 0.04 mv. In the poorly buffered solutions at the beginning of the titration, hydrogen electrodes ordinarily differed by 1 to 2 mv, but the emf difference dropped to 0.01 to 0.02 mv as soon as 1 ml of acid solution had been added.

In recognition of the deleterious effect of oxygen, both on hydrogen and on silver–silver-chloride electrodes, precautions were taken to exclude traces of air from the titration cell and from the acid-titrating solution. In some of the preliminary experiments, air was permitted to enter the burette as the acid solution was withdrawn. Before the end of the titration the effect of oxygen was evident in the slow attainment of equilibrium emf values and in the unsteadiness of the hydrogen electrodes. To obviate this source of error, the hydrogen that escaped from the cell while the hydrogen electrodes were being brought to equilibrium previous to the start of the titration was allowed to pass through the empty burette and the large test tube, *B*, by closing the stopcock between the trap, *G*, and the cell. In this way, air was removed from the burette, *C*, and it was prevented from gaining entrance to the burette during the titration by filling the funnel, *A*, with water. When the platinum electrodes had been allowed sufficient time for saturation with hydrogen, the burette was removed from the titration cell, and a vigorous stream of hydrogen was passed into *F* and out through the rubber stopper to prevent entrance of air into the cell. The burette was attached to the flask containing the acid solution, filled through its tip by hydrogen pressure, and replaced in the rubber stopper for the titrations. The burette was calibrated at intervals of 5 ml by weighing the amount of acid solution delivered.

Where a large number of emf measurements must be made without sacrifice of accuracy, as in an electrometric titration, rapidity of equilibrium is particularly desirable. If such a titration were performed in a cell without liquid junction by the addition of strong alkali to a solution of weak acid (or weak-acid–chloride mixture) as has been the usual practice when cells with liquid junction were used, the chloride-ion concentration would be progressively lowered, and the reference electrode would be slow to attain its new equilibrium potential after the addition of each increment of titrating solution. These measurements show that conditions of thermodynamic equilibrium between a small silver–silver-chloride electrode and the solution may be successfully met throughout the entire titration if oxygen is excluded and if the temperature, ionic strength, and chloride concentration are held constant.

The initial emf measurements, made before any acid solution had been admitted to the cell, drifted upward at a rate of several tenths of a millivolt per minute. After about 2 percent of the salt had been titrated, however, the cell attained a constant emf within 1 to 2 minutes following the addition of an increment of acid. This emf value rarely changed more than 0.1 mv when no more acid was added during the next 5 to 15 minutes. In one case, the cell was found to change 0.18 mv (corresponding to 0.003 pH unit) in 45 minutes. The entire titration usually required about 3 hours, when the acid was added at intervals of 10 minutes. If the titration is performed in an air bath or constant-temperature room, a longer time is required for

thermal equilibrium to be attained, since the heat of neutralization is dissipated but slowly under these conditions.

If neither the sodium or potassium salt of the weak acid is available, a sample of the free acid can be used. The acid should be neutralized carefully with standard alkali and the necessary amounts of water and solid sodium chloride added before the start of the titration with nitric acid. The neutralization can be performed electrometrically in the titration cell. Perchloric acid and sodium perchlorate can be substituted for nitric acid and potassium nitrate as components of the titrating solution if desired.

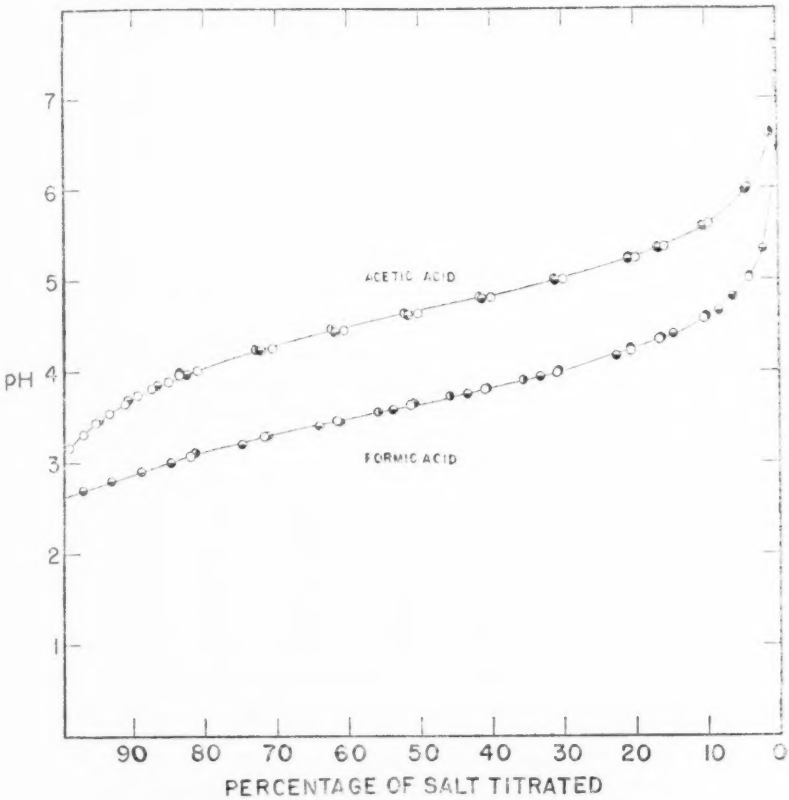

FIGURE 2.—pH–*titration curves for formic and acetic acids.*
The data of six experiments are represented.
◒=experiments 1 and 5; ○=experiments 2 and 4; ◑=experiments 3 and 6.

3. RESULTS AND CALCULATIONS

The results of three electrometric titrations of sodium formate and three of sodium acetate are summarized in tables 2 to 7. The emf values have been corrected to a hydrogen pressure of 760 mm. Experiment 1 was performed at 30° C, and the other five were carried out at 25° C in the water thermostat. The pH values were computed from eq 4, and pK' was derived from eq 7. Figure 2 is a plot of all the titration data for formic acid and acetic acid mixtures. The pH

values of the formate solutions in experiment 1 at 30° C were so close to those at 25° C that a single curve has been drawn through the results of all three experiments.

TABLE 2.—*Calculation of the dissociation constant of formic acid from electrometric titration of sodium formate with nitric acid reagent: experiment 1, 30° C*

[Millimoles of sodium formate=4.957, dissolved in 100 ml of 0.05-*m* sodium chloride solution; ionic strength constant, μ=0.0996; $-\log f_i$=0.115; $E^{\circ\prime}$=0.30425]

HNO_2	E	$(E-E^{\circ\prime})/k$ =pH	M_H	HA	A^-	$\log (M_A/M_{HA})$	pK'
Moles×10³	*Int. v*		*Moles*×10³	*Moles*×10³	*Moles*×10³		
0.000	0.7643	7.650					
.102	.62528	5.339	0.001	0.101	4.856	1.682	3.772
.207	.60532	5.007	.002	.205	4.752	1.365	3.737
.307	.59420	4.822	.002	.305	4.652	1.183	3.754
.409	.58585	4.683	.003	.406	4.551	1.050	3.748
.514	.57937	4.575	.004	.510	4.447	0.941	3.749
.714	.56958	4.413	.006	.708	4.249	.778	3.750
1.118	.55519	4.173	.010	1.108	3.849	.541	3.737
1.638	.54157	3.947	.018	1.620	3.337	.314	3.748
2.147	.53033	3.760	.028	2.119	2.838	.127	3.748
2.658	.51983	3.585	.044	2.614	2.343	−.047	3.747
3.173	.50920	3.408	.069	3.104	1.853	−.224	3.747
3.698	.49753	3.214	.110	3.588	1.369	−.418	3.747
4.196	.48515	3.008	.184	4.012	0.945	−.628	3.751
4.402	.47947	2.914	.232	4.170	.787	−.724	3.753
4.608	.47336	2.812	.297	4.311	.646	−.824	3.751
4.809	.46723	2.710	.381	4.428	.529	−.923	3.748
5.013	.46097	2.606	.490	4.523	.434	−1.018	3.739

TABLE 3.—*Calculation of the dissociation constant of formic acid from electrometric titration of sodium formate with nitric acid reagent: experiment 2, 25° C*

[Millimoles of sodium formate=4.965, dissolved in 100 ml of 0.05-*m* sodium chloride solution; ionic strength constant, μ=0.0997; $-\log f_i$=0.114; $E^{\circ\prime}$=0.30606]

HNO_3	E	$(E-E^{\circ\prime})/k$ =pH	M_H	HA	A^-	$\log (M_A/M_{HA})$	pK'
Moles×10³	*Int. v*		*Moles*×10³	*Moles*×10³	*Moles*×10³		
0.000	0.7839	8.081					
.203	.60272	5.016	0.001	0.202	4.763	1.363	3.767
.508	.57702	4.582	.004	.504	4.461	0.947	3.749
.815	.56304	4.345	.007	.808	4.157	.711	3.748
1.016	.55604	4.227	.009	1.007	3.958	.594	3.747
1.524	.54208	3.991	.016	1.508	3.457	.360	3.745
2.029	.53116	3.806	.025	2.004	2.961	.170	3.750
2.539	.52140	3.641	.039	2.500	2.465	−.006	3.761
3.050	.51096	3.465	.060	2.990	1.975	−.180	3.759
3.557	.50106	3.297	.090	3.467	1.498	−.365	3.776
4.066	.48901	3.077	.156	3.910	1.055	−.569	3.760

TABLE 4.—*Calculation of the dissociation constant of formic acid from electrometric titration of sodium formate with nitric acid reagent: experiment 3, 25° C*

[Millimoles of sodium formate=5.005, dissolved in 200 ml of 0.05-*m* sodium chloride solution; μ at beginning =0.0750, μ at end=0.0799; μ (average) =0.0775. $-\log f_i$=0.104; $E^{\circ\prime}$=0.30547]

HNO_2	E	$(E-E^{\circ\prime})/k$ =pH	M_H	HA	A^-	$\log (M_A/M_{HA})$	pK'
Moles ×10³	*Int. v*		*Moles* ×10³	*Moles* ×10³	*Moles* ×10³		
0.000	0.7346	7.256					
.200	.60347	5.039	0.002	0.198	4.807	1.385	3.758
.508	.57718	4.594	.007	.501	4.504	0.954	3.744
.811	.56345	4.362	.012	.799	4.206	.721	3.745
1.024	.55616	4.239	.016	1.008	3.997	.598	3.745
1.521	.54272	4.012	.028	1.493	3.512	.371	3.745
1.778	.53681	3.912	.035	1.743	3.262	.272	3.744
2.030	.53144	3.821	.044	1.986	3.019	.182	3.743
2.286	.52627	3.733	.054	2.232	2.773	.094	3.743
2.540	.52124	3.648	.067	2.473	2.532	.010	3.742
2.794	.51637	3.566	.081	2.713	2.292	−.073	3.743
3.049	.51138	3.482	.100	2.949	2.056	−.157	3.743
3.557	.50118	3.309	.149	3.408	1.597	−.329	3.742
4.066	.49012	3.122	.235	3.831	1.174	−.514	3.740

TABLE 5.—*Calculation of the dissociation constant of acetic acid from electrometric titration of sodium acetate with nitric acid reagent: experiment 4, 25° C*

[Millimoles of sodium acetate=4.984, dissolved in 100 ml of 0.05-*m* sodium chloride solution; ionic strength constant, $\mu=0.0998$; $-\log f_i=0.114$; $E^{\circ\prime}=0.30606$]

HNO_3	E	$(E-E^{\circ\prime})/k=pH$	M_H	HA	A−	$\log (M_A/M_{HA})$	pK'
Moles $\times 10^3$	*Int. v*		*Moles* $\times 10^3$	*Moles* $\times 10^3$	*Moles* $\times 10^3$		
0.000	0.7641	7.745					
.174	.66617	6.089	0.00	0.174	4.810	1.442	4.761
.477	.63860	5.623	.000	.477	4.507	0.975	4.762
.787	.62385	5.373	.001	.786	4.198	.728	4.759
.982	.61676	5.254	.001	.981	4.003	.611	4.757
1.489	.60261	5.014	.002	1.487	3.497	.371	4.757
1.994	.59102	4.818	.003	1.991	2.993	.177	4.755
2.505	.58034	4.638	.004	2.501	2.483	−.003	4.755
3.013	.56970	4.458	.006	3.007	1.977	−.182	4.754
3.521	.55818	4.263	.009	3.512	1.472	−.378	4.755
4.037	.54387	4.021	.015	4.022	0.962	−.621	4.756
4.133	.54058	3.966	.021	4.112	.872	−.673	4.753
4.239	.53675	3.901	.024	4.215	.769	−.739	4.754
4.343	.53261	3.831	.029	4.314	.670	−.809	4.754
4.444	.52799	3.753	.034	4.410	.574	−.885	4.752
4.537	.52313	3.670	.041	4.496	.488	−.965	4.749
4.649	.51649	3.558	.054	4.595	.389	−1.072	4.744
4.746	.50994	3.447	.070	4.676	.308	−1.181	4.742
4.839	.50255	3.322	.094	4.745	.239	−1.298	4.734
4.940	.49340	3.168	.134	4.806	.178	−1.431	4.713

TABLE 6.—*Calculation of the dissociation constant of acetic acid from electrometric titration of sodium acetate with nitric acid reagent: experiment 5, 25° C*

[Millimoles of sodium acetate =4.938, dissolved in 100 ml of 0.05-*m* sodium chloride solution; ionic strength constant, $\mu=0.0994$; $-\log f_i=0.114$; $E^{\circ\prime}=0.30606$]

HNO_3	E	$(E-E^{\circ\prime})/k=pH$	M_H	HA	A−	$\log (M_A/M_{HA})$	pK'
Moles$\times 10^3$	*Int. v*		*Moles*$\times 10^3$	*Moles*$\times 10^3$	*Moles*$\times 10^3$		
0.000	0.7590	7.659					
.206	.66154	6.011	0.000	0.206	4.732	1.361	4.764
.511	.63634	5.585	.000	.511	4.427	0.938	4.761
.816	.62251	5.351	.001	.815	4.123	.704	4.761
1.020	.61536	5.230	.001	1.019	3.919	.585	4.759
1.526	.60155	4.996	.002	1.524	3.414	.350	4.760
2.034	.58994	4.800	.003	2.031	2.907	.156	4.758
2.543	.57920	4.618	.004	2.539	2.399	−.025	4.757
3.051	.56840	4.436	.006	3.045	1.893	−.206	4.756
3.561	.55653	4.235	.009	3.552	1.386	−.409	4.758
4.069	.54153	3.982	.017	4.052	0.886	−.660	4.756
4.272	.53424	3.858	.023	4.249	.689	−.790	4.762
4.476	.52481	3.699	.039	4.437	.501	−.947	4.760
4.677	.51206	3.483	.064	4.613	.325	−1.152	4.749

TABLE 7.—*Calculation of the dissociation constant of acetic acid from electrometric titration of sodium acetate with nitric acid reagent: experiment 6, 25° C*

[Millimoles of sodium acetate =4.928, dissolved in 200 ml of 0.05-*m* sodium chloride solution; μ at beginning =0.075, μ at end =0.079, μ (average) =0.077; $-\log f_i=0.104$; $E^{\circ\prime}=0.30547$]

HNO_3	E	$(E-E^{\circ\prime})/k=pH$	M_H	HA	A−	$\log (M_A/M_{HA})$	pK'
Moles$\times 10^3$	*Int. v*		*Moles*$\times 10^3$	*Moles*$\times 10^3$	*Moles*$\times 10^3$		
0.000	0.7553	7.606					
.051	.69645	6.611	0.000	0.051	4.877	1.971	4.744
.206	.66073	6.007	.000	.206	4.722	1.360	4.751
.512	.63606	5.590	.001	.511	4.417	0.937	4.757
.821	.62205	5.353	.001	.820	4.108	.700	4.757
1.021	.61554	5.243	.002	1.019	3.909	.584	4.763
1.534	.60153	5.006	.003	1.531	3.397	.346	4.764
2.044	.58999	4.811	.005	2.039	2.889	.151	4.764
2.560	.57929	4.630	.007	2.553	2.375	−.031	4.765
3.069	.56870	4.451	.011	3.058	1.870	−.214	4.769
3.582	.55676	4.249	.016	3.566	1.362	−.418	4.771
4.097	.54197	3.999	.030	4.067	.861	−.674	4.777

In the fourth column of each table, M_H represents the number of moles of hydrogen ion in v ml of solution, where v is the total volume of solution in the titration cell. Thus $M_H \approx m_H v/1000$, where m_H is the molality of hydrogen ion computed from the pH value:

$$-\log m_H = \text{pH} + \log f_1. \quad (8)$$

The number of moles of weak acid, HA, given in the fifth column of each table, was obtained by subtracting M_H from the amount of nitric acid listed in the first column. The values of A^- (sixth column) are the differences between the amount of sodium salt used (given at the head of each table) and the amounts of HA.

The average pK' value for each experiment is given in table 8. The last two measurements of experiments 1 and 4, when more than 95 percent of the salt had been neutralized, have not been included in the average. The averages of all the pK' values derived from these experiments agree very well (0.001 unit) with the best values of pK for these two acids given in the literature [10, 11].

TABLE 8.—*Summary of* pK', pK, *and* K *for formic acid and acetic acid at 25° C*

Experiment number	avg pK'	μ	pK'−pK	pK	$K\times10^4$
FORMIC ACID					
1	[a] 3.751	0.1	0.01	[a] 3.741	[a] 18.2
2	3.756	.1	.009	3.747	17.9
3	3.744	.078	.007	3.737	18.3
Mean (25° C)				3.742	18.1
ACETIC ACID					
4	4.753	0.1	0.005	4.748	1.79
5	4.758	.1	.005	4.753	1.77
6	4.762	.077	.003	4.759	1.74
Mean (25° C)				4.754	1.77

[a] At 30°C.

Since pK' for many monobasic acids at an ionic strength of 0.1 differs but little from the value at zero ionic strength, it is probably unnecessary for practical work to make the large number of measurements requisite to an unambiguous extrapolation. For a check on the accuracy of the method, however, pK was computed from pK' by the application of extrapolation corrections taken from the careful measurements of the dissociation constant of formic acid by Harned and Embree [10] and of the dissociation constant of acetic acid by Harned and Ehlers [11]. These corrections, the amounts to be subtracted from pK', are given in the fourth column of table 8, and the pK values are listed in the fifth column. The dissociation constant, K, is listed in the sixth column. Harned and Embree found 3.752 and 3.753 for the pK values of formic acid at 25° and 30° C, respectively, and Harned and Ehlers have given 4.756 for the pK of acetic acid at 25° C.

It is evident that the electrometric titration, modified as described in this paper, may have consdiderable usefulness as a practical means of determining dissociation constants of weak monobasic acids and

pH values of buffer solutions with an accuracy of 0.01 to 0.02 unit. By substitution of a glass or quinhydrone electrode, the application of the method can be extended to many systems in which the hydrogen electrode cannot be used.

Titration curves and dissociation constants of weak polybasic acids at constant ionic strength can be obtained by modifications of the method described here. To obtain data for the second, third, etc., groups, the corresponding salt is titrated in sodium chloride solution with nitric acid solution to which has been added sodium chloride and sufficient potassium nitrate to compensate for the decrease in ionic strength during the titration. As an alternate procedure, a disodium salt can be titrated with a solution of acid sulfate and sodium chloride which contains enough neutral salt to compensate for the decrease in ionic strength and to maintain a constant concentration of bivalent ions, e. g., sulfate. The pH values in the range governed by the first dissociation constant are then obtained, as described in this paper, by the titration of the acid salt of the weak acid with nitric acid reagent. The determination of the concentration and dissociation constant of each acid group in a mixture [14] is improved by use of this procedure.

The titration method as outlined is not well adapted for use over a wide range of temperatures. It cannot conveniently furnish the accurate data over a wide range of ionic strengths which are required to determine a_t and β parameters. Wherever it can be used, however, it represents a considerable improvement over a pH assembly with liquid junction.

Because of these limitations, the electrometric titration method is unsuitable for the precise determination of dissociation constants and pH values of buffer standards. When an accuracy within 0.003 unit is desired, the emf method described in earlier papers from this Bureau [6, 7, 12] should be employed. The improved titration should be regarded rather as a rapid method of establishing dissociation constants and practical buffer standards for pH control where an uncertainty of 0.02 unit is permissible.

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FUNCTION OF CARBON DIOXIDE IN PRODUCING EFFLORESCENCE ON PLASTER AND CEMENT PRODUCTS

By Dana L. Bishop

ABSTRACT

Hydrated magnesium sulfate was identified as the principal compound in efflorescence on white-coat plaster finish. This salt is not a constituent of the white-coat backing but is formed by reactions involving gypsum and magnesia in the plaster, carbon dioxide from the air, and water. The reaction to form magnesium sulfate cannot take place until after the $Ca(OH)_2$ has been changed to $CaCO_3$. Magnesium sulfate efflorescence may also be formed on cement products by the same reactions.

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I. INTRODUCTION

Efflorescence is defined as the deposit of crystalline salts on the surface of masonry or plaster. These salts are usually present in the interior of the masonry or plaster and are dissolved by water and transported to the surface, and there redeposited by evaporation of the water, with consequent recrystallization of the salts. For efflorescence to occur, there must be both soluble salts and water to dissolve and transfer the salts. Efflorescence is frequently associated with and may be the cause of disintegration of the surface of plaster.

One type of efflorescence occurring on plaster consists chiefly of magnesium sulfate, which is not a constituent of the plaster. In order to determine the origin of the salt, some experiments were performed on the individual constituents and mixtures having the composition of white-coat plaster. The results are given in the report.

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II. EFFLORESCENCE ON PLASTER

1. CHEMICAL CONSTITUENTS OF PLASTER AND EFFLORESCENCE

Plaster ordinarily consists of a base coat of gypsum and sand and a finish coat of gypsum and hydrated lime. The hydrated lime may be either a high-calcium or a dolomitic type, the latter being used in a majority of the finish-coat plasters. The principal chemical constituents of set plaster (aside from the sand, which has a very low solubility in water) are $CaSO_4.2H_2O$, $Ca(OH)_2$, MgO, and $Mg(OH)_2$.

The $Ca(OH)_2$ combines with CO_2 from the air to form $CaCO_3$, the reaction proceeding slowly in normally dry plaster but more rapidly when the optimum amount of moisture is present. The extent of carbonation of the hydrated lime varies greatly and frequently is unrelated to the age of the plaster, as shown by the analyses of many plasters. For example, samples from some buildings 30 years old contained about equal quantities of $CaCO_3$ and $Ca(OH)_2$, whereas all or nearly all of the $Ca(OH)_2$ was converted to $CaCO_3$ in other samples from buildings much less than 30 years old. Regions may exist anywhere in plaster, but especially at the surface, where $Ca(OH)_2$ has been completely carbonated.

The composition of a sample of efflorescence on plaster, computed from an analysis, was as follows:

	Percent
$MgSO_4.7H_2O$	73.3
$Mg(OH)_2$	5.7
$CaSO_4.2H_2O$	12.8
$CaCO_3$	5.9
$Ca(OH)_2$	2.1

2. FORMATION OF NESQUEHONITE

Complete conversion of $Ca(OH)_2$ to $CaCO_3$ had not occurred in the majority of plasters analyzed. In a few samples, however, the amounts of CO_2 found were enough to carbonate the total contents of $Ca(OH)_2$ and MgO. Furthermore, some samples contained MgO, CO_2, and chemically combined water in the molar ratios corresponding to those of the mineral nesquehonite, $MgCO_3.3H_2O$. The chemical evidence (by W. F. Clarke, of this Bureau) for the existence of this compound in plaster was confirmed by microscopical and X-ray analyses.

Johnston [1] [1] and Kline [2], respectively, showed that $MgCO_3.3H_2O$ in water remains the stable phase, at 16° and 25° C, as long as the air in contact with the water contains at least 0.04 percent of CO_2. They found that when the concentration of CO_2 was less than 0.04 percent, the $MgCO_3.3H_2O$ changed very slowly to $Mg(OH)_2$. Johnston indicated that at higher temperatures $MgCO_3.3H_2O$ would be the stable phase only at higher concentrations of CO_2. While the CO_2 content of the outside air is ordinarily about 0.04 percent, that of the air inside of buildings is variable and often much greater. The concentration may reach 0.1 percent or more, well above that at which $MgCO_3.H_2O$ is stable.

[1] Figures in brackets indicate the literature references at the end of this paper.

3. REACTION OF NESQUEHONITE WITH GYPSUM

Some information regarding the possibility that nesquehonite, gypsum, and lime react in moist plaster may be obtained from the respective solubilities of these compounds given in table 1.

TABLE 1.—*Solubilities of some compounds occurring or formed in plaster*

Compound	Solubility		Temperature	Reference
	g/kg	*g mole/kg*	*°C*	
$CaSO_4.2H_2O$	2.082	121×10^{-4}	25	[3]
$Ca(OH)_2$	1.464	198	25	[4]
$MgCO_3.3H_2O$	1.874	136	25	[2]
$Mg(OH)_2$	0.027	4.6	25	[5]
$CaCO_3$	.066	6.6	16	[1]

The solubility relations of $CaSO_4.2H_2O$ and $MgCO_3.H_2O$ are such that the following reaction will proceed toward the right, since $CaCO_3$ is relatively insoluble:[2]

$$CaSO_4.2H_2O+MgCO_3.3H_2O+2H_2O\rightleftharpoons CaCO_3+MgSO_4.7H_2O. \quad (1)$$

The other product of this reaction, $MgSO_4.7H_2O$, is the chief constituent of efflorescence on plaster.

Tests were made to determine whether or not the reaction products indicated by equation 1 could be produced when a water suspension of MgO and $CaSO_4.2H_2O$ was exposed to CO_2 from the air. After several days small crystals were observed at the surface of the solution. These crystals were shown to be $CaCO_3$ by microscopical analysis. The reaction proceeded slowly, and at 7 months, chemical analysis of the sediment indicated that nearly all the MgO had been changed to $MgSO_4.7H_2O$. In another test $MgSO_4.7H_2O$ was produced in a few hours by bubbling CO_2 through a suspension of MgO and $CaSO_4.2H_2O$. It was formed also when air was bubbled through a similar suspension, the experiment being conducted at 30° C near an open window in a large laboratory ($30\times45\times12$ ft) with all gas burners shut off. The CO_2 concentration of the air used in this test was probably near that of the outside air. It would appear therefore that $MgSO_4.7H_2O$ could be formed in plaster by the action of CO_2 and water on the constituents gypsum and hydrated dolomitic lime.

While these reactions take place readily in solution, ideal conditions seldom exist for rapid reaction in ordinary plaster for two reasons. First, adequate amounts of water often are not present. Second, $MgCO_3.3H_2O$ can not be formed in contact with $Ca(OH)_2$ because they react, yielding insoluble $Mg(OH)_2$ and $CaCO_3$. This explains why $MgCO_3.3H_2O$ is so rarely found in ordinary plaster.

Since $MgCO_3.3H_2O$ is the intermediate product in the production of $MgSO_4.7H_2O$, $Ca(OH)_2$ must be changed to $CaCO_3$ before $MgSO_4.7H_2O$ also can be produced.

Obviously, equilibrium is seldom established throughout a plaster, and in obtaining a sample of efflorescence it is difficult sometimes to keep from contaminating the efflorescence with compounds that would not be present if equilibrium had been established. This accounts for the presence of $Ca(OH)_2$ in the analysis of the efflorescence sample previously given.

[2] Hydrates are indicated in the equation to avoid the impression that anhydrite and magnesite occur in plaster.

4. EFFECT OF CARBON DIOXIDE AND WATER ON WHITE-COAT SAMPLES

Having demonstrated that MgO and $CaSO_4.2H_2O$, in a water suspension, can react with CO_2 to form $MgSO_4$, an attempt was made to produce efflorescence on specimens of white-coat plaster. Prisms having the composition of white-coat plaster were prepared from 2 parts by weight of dolomitic hydrated lime and 1 part of calcined gypsum. Similar prisms were prepared from a high-calcium hydrated lime and calcined gypsum. These specimens were then subjected to moisture and CO_2 by storing them in a closed cylinder over but not in contact with water and introducing CO_2 from a cylinder of compressed CO_2 gas until a pressure of 50 pounds per square inch was attained. The specimens were kept in the cylinder for a day and were then removed and allowed to dry in the laboratory. After 10 cycles of alternate treatments with moist CO_2 and dry air, a profuse efflorescence similar in appearance and composition to that found on plaster had developed in the specimens prepared with the dolomitic hydrated lime (fig. 1, specimens 440 to 447). No efflorescence, however, appeared on the identically treated specimens (457 to 459) containing high-calcium hydrated lime.

Although efflorescence did not appear on the white-coat samples composed of a high-calcium lime and gypsum, it cannot be concluded that trouble other than efflorescence may not ensue when high-calcium limes are used, for it is a well-known fact that ultimately the continual presence of moisture is detrimental to almost any type of plaster.

5. VOLUME CHANGES

The disintegration of the white coat during efflorescence is not surprising if consideration is given to the large increase in volume accompanying the conversion of the plaster constituent MgO to $MgSO_4.7H_2O$. The following computed net volume increases, occurring with the production of the various magnesium compounds in the process, were obtained from the data in table 2: MgO to $Mg(OH)_2$, 124 percent; MgO to $MgCO_3.3H_2O$, 585 percent; and MgO to $MgSO_4.7H_2O$, 1,280 percent. Such large increases in volume account for the disintegration of the plaster, even though the change of MgO to $MgSO_4.7H_2O$ may be incomplete.

TABLE 2.—*Molecular volumes of some compounds found in plaster and efflorescence*

Compound	Molecular weight	Density	Molecular volume
		g/ml	*ml*
MgO	40.32	3.7	10.9
$Mg(OH)_2$	58.34	2.38	24.4
$MgCO_3.3H_2O$	138.38	1.85	74.8
$MgSO_4$	120.38	2.66	46.5
$MgSO_4.7H_2O$	246.49	1.64	150.2

6. RECOMMENDATIONS RELATING TO PREVENTION OF EFFLORESCENCE ON PLASTER

Moisture is essential for the formation of efflorescence on plaster. Even though efflorescence may not appear, moisture is very detri-

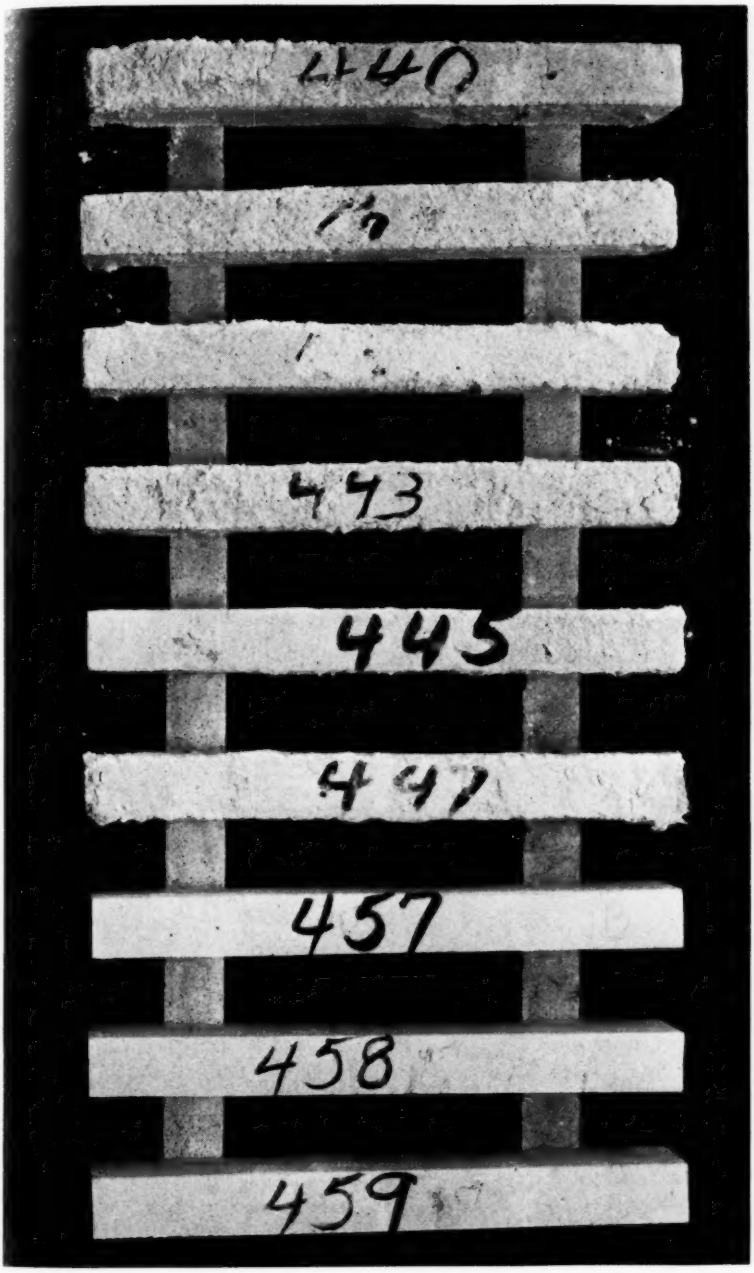

FIGURE 1.—*Efflorescence produced experimentally by the action of water and carbon dioxide on plaster samples.*

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mental to any plaster and leads to the disintegration of the plaster and to rotting of adjacent wood. In general, adequate protection from moisture over the greater portions of plaster has been considered in the design of buildings. Unfortunately, faulty design has resulted in certain areas of plaster becoming repeatedly moist. In such instances efflorescence appears. Plaster applied directly to outside masonry walls may become damp because of condensation of moisture. Furred walls should eliminate this source of trouble. The furring not only tends to keep the temperature of the plaster above the dew point but also diminishes the transfer of water from leaking walls to the plaster. Ventilation of insulated walls furnishes a means of escape for water accumulating in the cold insulation. Insulation containing moisture in contact with plaster produces conditions favoring the formation of $MgCO_3.3H_2O$ and $MgSO_4.7H_2O$. Unless cold-water pipes passing through plastered walls are provided with sleeves, the condensed moisture may collect in the adjacent plaster and produce efflorescence.

III. MAGNESIUM SULFATE EFFLORESCENCE ON CEMENT PRODUCTS

Magnesium sulfate efflorescence has been observed also on cement mortar, cinder block, and other cement products. Since $CaSO_4$ and MgO are among the constituents of cement, it is possible that they may react in the prescence of CO_2 and moisture to form $MgSO_4$.

In order to determine the combined action of CO_2 and water in extracting MgO and SO_3 from a cement, CO_2 was bubbled through a water suspension of a cement and the solid phase analyzed. In 3 days the MgO content of the solid phase was reduced from 4.7 to 2.0 percent and the SO_3 content from 1.8 to 0.6 percent.

Tricalcium sulfoaluminate, $3CaO.Al_2O_3.3CaSO_4.31H_2O$, formed during the setting of cement contains $CaSO_4$ but is a much less soluble compound than gypsum, $CaSO_4.2H_2O$. In experiments to determine if sulfate could be extracted from tricalcium sulfoaluminate, CO_2 was passed through a water suspension of this compound and the solids were examined microscopically. After a short time, the precipitation of $Al(OH)_3$ and $CaCO_3$ indicated the decomposition of tricalcium sulfoaluminate had made available $CaSO_4$ for reaction with $MgCO_3$ $3H_2O$. It was found also that the sulfoaluminate could be decomposed by bubbling air of normal CO_2 concentration through the suspension. It would appear, therefore, that $MgSO_4$ efflorescence might arise also from the reaction of CO_2 and water with the magnesia and sulfate-bearing compounds in cement.

No attempt was made to produce efflorescence on cement experimentally. However, some interesting information was obtained from an investigation conducted by Rogers and Blaine [6], who reported on the efflorescence on mortars prepared from 41 commercial masonry cements. Their mortar specimens were immersed in water for 72 hours in order to determine the absorption. Such treatment would be expected to remove much of the readily soluble salts. The specimens were then placed on end in a tray of water to a depth of one-half inch. Observations for efflorescence at the end of 3 months were reported. The composition of the efflorescence was not determined. It is interesting to note that their mortars showing no efflorescence had an average

MgO content of 5.0 percent, those with slight efflorescence 8.8 percent, and those showing pronounced efflorescence 19.7 percent.[3]

The amount of $MgSO_4.7H_2O$ formed in cement products would be limited by the amount of sulfate or magnesia present. Magnesia might be extracted also by water and CO_2 from magnesium carbonate in the sand or aggregate. Magnesium chloride also might be formed from reaction of $CaCl_2$ with $MgCO_3.3H_2O$.

IV. SUMMARY

Hydrated magnesium sulfate was identified as the principal constituent of efflorescence on plaster. Its formation was accounted for by reactions involving magnesia and gypsum in the plaster, CO_2 from the air, and moisture. This type of efflorescence was observed also on some cement products.

Magnesium sulfate was produced experimentally by the action of CO_2 on a water suspension of MgO and $CaSO_4.2H_2O$.

Hydrated magnesium sulfate efflorescence was formed on white-coat plaster specimens containing dolomitic hydrated lime and gypsum when treated with moist CO_2 and then allowed to dry. The disintegration accompanying the efflorescence was explained by the large volume changes involved in the formation and crystallization of $MgCO_3.3H_2O$ and $MgSO_4.7H_2O$.

If plaster is kept dry, no trouble with efflorescence is experienced, because moisture is necessary to transfer the salts to the surface and to take part in the reaction. Plaster, therefore, should be protected from moisture by keeping it above the dew point. Moisture accumulations from various sources, such as transmission through pervious walls and leaks from water and steam pipes, should be prevented.

Magnesium sulfate also is found as efflorescence on concrete, possibly being derived from MgO and sulfate in the cement by reaction with CO_2 and water. The compound $3CaO.Al_2O_3.3CaSO_4.31H_2O$, a constituent of set cement is decomposed by CO_2 and water, making the $CaSO_4$ available for reaction with $MgCO_3.3H_2O$ to form soluble $MgSO_4$.

The author is indebted to W. F. Clarke for the chemical evidence and to H. F. McMurdie for the X-ray evidence that nesquehonite occurs in plaster.

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WASHINGTON, February 5, 1943.

[3] The chemical analyses for cements 38 and 39 are interchanged in table 1 of reference [6]. Also, the SO_3 reported for their sample 1 appears to have been determined on a sample that had been ignited with a blast lamp, which would result in the loss of SO_3 and alkalies. Redetermination of SO_3 on a sample not ignited gave 2.6 percent.

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STUDY OF THE SYSTEM CaO-Al_2O_3-H_2O AT TEMPERATURES OF 21° AND 90° C

By Lansing S. Wells, W. F. Clarke, and H. F. McMurdie

ABSTRACT

A study has been made of the system CaO-Al_2O_3-H_2O at temperatures of 21° and 90° C. Diagrams have been constructed showing the solubility relations of the various phases at these temperatures. The solid phases were investigated by petrographical and X-ray diffraction methods. By means of X-ray diffraction patterns, it was found that the so-called hexagonal tricalcium aluminate hydrate is in reality a mixture of hexagonal $2CaO.Al_2O_3.8H_2O$ and hexagonal $4CaO.Al_2O_3.13H_2O$ intercrystallized in equimolecular proportions. On standing at room temperature, dry dicalcium aluminate hydrate is slowly converted into the tetracalcium aluminate hydrate and hydrated alumina. Loss of water of hydration in the tetracalcium aluminate hydrate results in a decrease in the unit cell along the *c* axis. Although the hexagonal di- and tetracalcium aluminate hydrates exist only as metastable phases in the system between 21° and 90° C, their approximate solubility relationships were ascertained at 21° C. As the temperature increases, the hexagonal aluminates become less stable. The only stable phases that occur in the system CaO-Al_2O_3-H_2O at atmospheric pressure over the temperature range of 21° to 90° C are gibbsite ($Al_2O_3.3H_2O$), the isometric tricalcium aluminate hexahydrate ($3CaO.Al_2O_3.6H_2O$), and $Ca(OH)_2$. The solubility curves of these three stable phases in the system CaO-Al_2O_3-H_2O were determined at 21° and 90° C. Over this temperature range, gibbsite is the stable phase up to a concentration of 0.33 g of CaO per liter; at concentrations greater than this, $3CaO.Al_2O_3.6H_2O$ is the stable phase until those points are reached at which $Ca(OH)_2$ also appears as a solid phase. The series of invariant points for gibbsite and the isometric phase occur at a concentration of 0.33 g of CaO per liter, but with the concentration of Al_2O_3 increasing from 0.02 g of Al_2O_3 per liter at 21° C to 0.11 g of Al_2O_3 per liter at 90° C.

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I. INTRODUCTION

The extensiveness of the literature pertaining to the hydrated calcium aluminates shows the scientific interest and technological importance which have been attached to these compounds. An experimental study of the system CaO-Al_2O_3-H_2O should possess considerable practical value not only for its direct bearing on the setting of high-alumina cements (which are composed largely of anhydrous calcium aluminates) and portland cements, but also for possible applications in the fields of geology, soil equilibria, water purification, and the extraction of purified hydrated alumina from crude bauxite.

The study of the system CaO-Al_2O_3-H_2O presents many difficulties, including:

1. The existence of numerous highly hydrated compounds, the determination of the degree of hydration of which is often a problem in itself.
2. The relatively low solubility of these compounds.
3. The fact that most of the compounds are metastable, yet, once formed, persist over long periods of time.
4. The close similarity in crystal habit and optical properties of the compounds occurring as thin hexagonal (or pseudohexagonal) plates.
5. The necessity for the rigid exclusion of carbon dioxide of the air.

II. GENERAL PROCEDURE

Only by approaching equilibrium in a number of different ways can any conclusive results be obtained in a system of the type of CaO-Al_2O_3-H_2O in which a number of metastable phases occur.

In order to study the phases that precipitate from supersaturation at 21° C, the first step was to prepare rather large quantities of metastable monocalcium aluminate solutions by shaking, for an hour or so, either anhydrous calcium aluminates less basic than tricalcium aluminate or alkali-free calcium aluminate cements with distilled water in the proportion of 50 g of solid to 1 liter of water. The mixtures then were filtered rapidly through a Büchner funnel. Samples of the clear filtrates were taken at once for chemical analysis. By this procedure, as was shown in a previous publication [1],[1] metastable solutions which contained up to 2.4 g of Al_2O_3 and 1.4 g of CaO per liter were obtained.

These clear, filtered solutions were then mixed in various proportions with solutions of calcium hydroxide of known concentration in the preparation of several series of reaction mixtures containing at least 2 liters of solution. Since precipitation of minute cyrstals started, in many instances, almost immediately upon the addition of the

[1] Figures in brackets indicate the literature references at the end of this paper.

calcium hydroxide solutions to the metastable calcium aluminate solutions, it was impossible to secure samples of the mixtures at this stage. But, inasmuch as care had been taken to measure out the volumes of the component solutions and to exclude CO_2, the initial compositions of the resultant mixtures were known accurately. The mixtures were set aside, for further observations, in tightly stoppered flasks in a room maintained at 21°±1° C. This same general procedure was followed in a previous study of the system CaO-SiO_2-H_2O [2].

A separation of solid phases occurred rapidly at first, and then more slowly, as the solutions changed from unstable states to conditions more nearly approaching equilibrium. The mixtures were shaken from time to time to facilitate an approach to equilibrium. Small samples of the precipitated material were removed at intervals for microscopical examination to follow any change in the solid phases which might be occurring. By this procedure it became evident that a phase which first appeared, in turn, often disappeared with the formation of a new phase as equilibrium was approached. Obviously, the problem was to establish the boundaries of the fields where the various metastable and stable phases precipitated from solution.

Having approached equilibrium by precipitation from supersaturation at 21° C, the next step was to determine whether the same equilibrium conditions could be attained from undersaturation. In these cases the solid phases were placed in calcium hydroxide solutions of varied concentrations, and the changes in both the aqueous and solid phases were followed.

Attempts also were made to reach equilibrium by lowering the temperature of the mixtures from higher temperatures to 21° C.

In all of these studies it was essential that the identity of the solid materials be established not only by chemical analysis, but also, whenever possible, by their optical properties. But, inasmuch as many of the products could not be identified definitely by optical means, it was necessary to obtain X-ray diffraction patterns.

The same procedures, except as noted otherwise, were used in studying the system at 90° C as at 21° C.

In the chemical analyses, the filtered solutions were made acid with hydrochloric acid, and the aluminum was precipitated as the hydroxide, redissolved, reprecipitated, and ignited to the oxide, according to Blum's method [3]. The calcium was precipitated as the oxalate, ignited to constant weight in a platinum crucible over a Meker burner, and weighed as the oxide. The solid phases, unless otherwise stated, were washed with alcohol and ether and then dried over calcium chloride in a desiccator and analyzed chemically for lime, alumina, and water (loss on ignition). It was often preferable to make the analyses for alumina and lime on samples other than those used for the determination of loss on ignition, because heat converted a portion of the alumina to a form difficultly soluble in acids. Blank eleterminations for alumina and lime were made for the reagents used and the proper corrections were applied.

Although these were the general procedures followed in this investigation, it will be necessary, as the occasion arises, to give more specific details.

III. STUDIES OF THE SYSTEM CaO-Al_2O_3-H_2O AT 21° C

1. HEXAGONAL HYDRATED CALCIUM ALUMINATES IN THE SYSTEM AT 21° C

Consideration will now be given to the studies of the metastable hexagonal hydrated calcium aluminates,[2] leaving those pertaining to the stable isometric form and hydrated alumina for later discussion.

The results of the studies are being presented in several arbitrarily chosen parts. The first deals primarily with the molar ratio, CaO/Al_2O_3, in the hexagonal hydrated calcium aluminates; the second with the water content of the products; the third with their optical properties; the fourth with their structure as revealed by X-ray data; and the fifth with a brief discussion of some conclusions which seem warranted. The real significance of the hexagonal hydrated calcium aluminates in the system CaO-Al_2O_3-H_2O can be appreciated only after the investigations of the other phases have been presented.

(a) MOLAR RATIO, CaO/Al_2O_3, IN THE HEXAGONAL CALCIUM ALUMINATES

Table 1 gives data pertaining to the hexagonal hydrated calcium aluminates obtained by approaching equilibrium from supersaturation. Column 5 shows the time that elapsed between the preparation of the initial unstable solutions and the subsequent filtration occasioned by the appearance of microscopically detectable quantities of solid phases other than the hexagonal hydrated calcium aluminates. The time ranged from 1 to 309 days. In 22 of 48 preparations, this was less than 10 days. The molar ratios, CaO/Al_2O_3, in the precipitates, as given in column 9, were calculated from the differences between the compositions of the unstable solutions before precipitation (columns 2 and 3) and after precipitation (columns 6 and 7). The molar ratios—CaO/Al_2O_3 (column 10) and H_2O/Al_2O_3 (column 11)—were computed from direct analyses of the solid phases that had been dried over $CaCl_2$. The indices of refraction of these solid phases (columns 12 and 13) were determined at the time the analyses were made.

In figure 1 the compositions of the initial solutions are represented by closed circles. Broken lines from these points to open circles connect the initial and final compositions. The numbers accompanying these lines give the molar ratios, CaO/Al_2O_3, in the precipitated hexagonal hydrated calcium aluminates as calculated from the differences in composition between the initial and final solutions (see table 1, column 9).

A curve, *ABD*, has been drawn primarily to facilitate the discussion of the solubility relations of these hexagonal hydrated calcium aluminates. Because the hexagonal aluminates were formed from supersaturation, it was felt that this curve should be passed through those points that indicated the more extensive precipitation rather than through the average of the points. *D* pertains to a composition

[2] In this paper the plate form will be designated as the hexagonal form, since the crystals appeared as thin hexagonal plates. In general, the crystals were too small to obtain satisfactory interference figures with a petrographic microscope to determine whether the crystals were uniaxial, and hence actually hexagonal. The tendency to form hexagonal (or pseudohexagonal) plates was so marked that, in those instances in which the interference figures revealed that the crystals were biaxial negative, the hexagonal configuration of the plates still persisted.

TABLE 1.—*Solubility relations pertaining to the hexagonal hydrated calcium aluminates as ascertained by an approach from a state of supersaturation at a constant temperature of 21°C, together with the refractive indices of the hexagonal aluminates thus formed.*

Experiment	Composition of initial solutions			Time to approach metastable equilibrium[a]	Composition of resulting solutions			Composition of hexagonal aluminates			Indices of refraction of hexagonal aluminates	
	Al_2O_3	CaO	Molar ratio, CaO/Al_2O_3		Al_2O_3	CaO	Molar ratio, CaO/Al_2O_3	Molar ratio, CaO/Al_2O_3 (calculated)	Molar ratio, CaO/Al_2O_3 (analysis)	Molar ratio, H_2O/Al_2O_3 (analysis)	ω	ϵ
1	2	3	4	5	6	7	8	9	10	11	12	13
	g/liter	*g/liter*		*Days*	*g/liter*	*g/liter*						
1	1.003	0.998	1.81	5	0.512	0.440	1.56	2.07	1.99	5.62	1.535	1.523
2	0.793	.764	1.75	5	.505	.445	1.60	2.01	1.99	5.90	1.534	1.524
3	.620	.600	1.76	1	.465	.435	1.70	2.04				
4	1.036	1.186	2.08	3	.367	.432	2.10	2.07	2.05	6.54	1.532	1.520
5	0.797	0.935	2.13	4	.364	.438	2.19	2.09	2.03	5.93	1.534	1.524
6	.587	.714	2.21	9	.345	.432	2.28	2.12	2.12	6.15	1.534	1.523
7	.798	1.052	2.40	3	.285	.449	2.86	2.14	2.09	5.93	1.535	1.525
8	.589	0.809	2.50	9	.267	.434	2.95	2.12	2.13	6.05	1.534	1.521
9	.556	.775	2.53	130	.286	.463	2.94	2.10	2.18	6.31		
10	.472	.708	2.73	138	.244	.436	3.25	2.17			1.535	1.520
11	.795	1.108	2.53	3	.262	.457	3.17	2.22	2.16	6.07	1.537	1.520
12	.592	0.868	2.66	9	.238	.451	3.44	2.14	2.10	6.47	1.533	1.520
13	.400	.663	3.01	142	.221	.439	3.61	2.27	2.22	7.00	1.532	1.517
14	.433	.697	2.99	57	.216	.438	3.69	2.20	2.18	6.16	1.530	1.520
15	.504	.813	2.93	1	.208	.458	4.00	2.20				
16	.576	.946	2.98	70	.201	.481	4.35	2.25	2.17	5.97	1.533	1.521
17	.400	.731	3.33	133	.201	.470	4.25	2.39	2.29	7.02	1.528	1.516
18	.762	1.196	2.85	70	.195	.466	4.34	2.34	2.33	7.03	1.535	1.515
19	.577	0.984	3.10	70	.185	.496	4.87	2.26	2.21	6.17	1.538	1.522
20	.400	.766	3.48	133	.188	.485	4.70	2.41	2.34	7.37	1.535	1.514
21	.708	1.174	3.02	57	.171	.488	5.22	2.32	2.21	6.33	1.535	1.510
22	.318	0.702	4.02	36	.154	.495	5.86	2.29			1.535	1.512
23	.575	1.045	3.30	69	.167	.530	5.77	2.40	2.29	6.22	1.534	1.523
24	.400	0.828	3.77	142	.169	.509	5.49	2.51	2.40	7.34	1.536	1.517
25	.609	1.164	3.48	309	.149	.506	6.17	2.60	2.43	6.63		
26	.400	0.886	4.03	133	.154	.528	6.19	2.64	2.42	7.59	1.533	1.516
27	.501	1.103	4.00	142	.130	.508	7.10	2.91	2.62	8.05		
28	.400	0.950	4.32	123	.146	.542	6.74	2.92	2.77	8.51	1.533	1.514
29	.557	1.210	3.95	70	.127	.523	7.48	2.91	2.63	8.00	1.537	1.515
30	.400	1.001	4.55	70	.116	.550	8.67	2.93				
31	.454	1.150	4.79	7	.113	.595	9.59	2.96	2.97	8.25	1.535	1.518
32	.181	0.704	7.08	56	.112	.586	10.4	3.12			1.530	1.510
33	.440	1.161	4.80	17	.096	.587	11.1	3.03	3.01	8.88	1.535	1.517
34	.394	1.168	5.39	17	.100	.614	11.2	3.43	3.45	10.98	1.538	1.515
35	.388	1.154	5.41	7	.104	.620	10.8	3.42		9.98	1.538	1.519
36	.286	0.993	6.32	48	.078	.614	14.3	3.32	3.54	11.25	1.540	1.517
37	.394	1.237	5.70	121	.090	.631	12.7	3.62	3.67	12.00	1.542	1.520
38	.241	0.939	7.08	56	.091	.658	13.1	3.40	3.73	12.25		
39	.348	1.175	6.14	8	.083	.639	16.9	3.68	3.69	11.57	1.530	1.511
40	.337	1.215	6.56	7	.067	.644	17.5	3.75			1.540	1.521
41	.302	1.183	7.12	6	.070	.687	17.8	3.85	3.82	11.98	1.530	1.511
42	.256	1.190	8.44	6	.042	.732	31.7	3.89	3.81	12.07	1.533	1.512
43	.219	1.227	10.2	8	.028	.813	52.7	3.94	3.94	12.60	1.541	1.523
44	.174	1.204	12.6	8	.025	.870	63.3	4.07	3.97	13.94	1.547	1.512
45	.164	1.239	13.7	8	.019	.914	87.6	3.99			1.545	1.521
46	.109	1.239	20.7	8	.012	1.032	156.0	3.88	3.68	10.83	1.550	1.520
47	.094	1.221	23.6	39	.012	1.047	159.0	3.96	3.97	12.01	1.550	1.520
48	.055	1.244	41.1	8	.006	1.132	342.0	4.16	3.97	13.00		

[a] Time which elapsed between the preparation of the initial unstable solutions and the subsequent filtration occasioned by the appearance of microscopically detectable quantities of solid phases other than metastable hexagonal hydrated calcium aluminates.

at a concentration of lime somewhat greater than that of a solution in equilibrium with coarsely crystalline $Ca(OH)_2$ as indicated by C (equivalent to 1.15 g of CaO per liter).

In general, the increase in lime in solution is accompanied by a decrease in alumina, and a more or less gradual increase from 2 to 4 in the molar ratio, CaO/Al_2O_3, in the solid phases. It is evident that there are no extensive sections along the curve *ABD* where the molar ratios, CaO/Al_2O_3, of the solid phases are exactly 2.0, 3.0, or

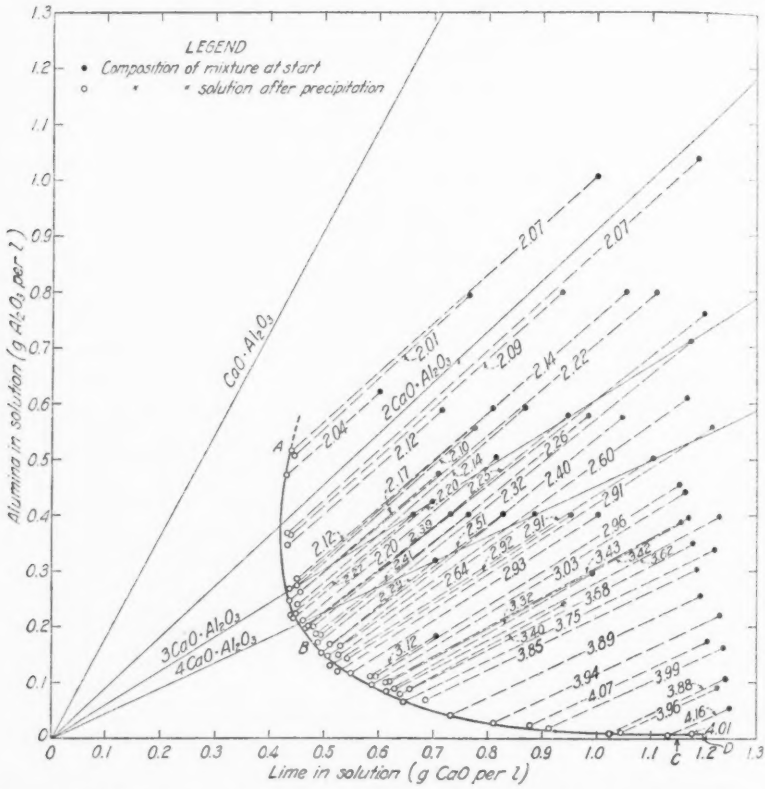

FIGURE 1.—*Quantity of alumina in solutions of increasing lime concentrations that are saturated with respect to metastable hexagonal calcium aluminate hydrates containing lime and alumina in the molar proportions shown: temperature, 21° C.*

4.0, such as would characterize a series of separate and distinct solubility curves of a hydrated dicalcium, tricalcium, or tetracalcium aluminate.

It is significant, however, that all the initial solutions having molar ratios, CaO/Al_2O_3, less than 2 gave rise to precipitates having molar ratios that approximated 2. Furthermore, although there was no instance in which the composition of the initial solution was exactly on the $2CaO.Al_2O_3$-composition line, yet, from experiment 4 of table 1, it can be seen that the molar ratios, CaO/Al_2O_3, of the unstable initial solution, of the precipitated solid phase, and of the resulting solution were all very close to 2.

Initial solutions having molar ratios greater than 2.1 produced precipitates having molar ratios less than the respective original solutions. Those initial solutions whose compositions were either on or very close to the $3CaO.Al_2O_3$-composition line (experiments 13, 14, 15, 16, and 21 of table 1) yielded solid phases whose molar ratios, CaO/Al_2O_3, were much less than 3 (ranging from 2.20 to 2.32). There may be considered to be a small section on the curve *ABD*, where the molar ratios, CaO/Al_2O_3, of the solid phases precipitated were approximately 3, but the molar ratios of the initial solutions from which these solid phases precipitated were, in general, greater than 4. There is a somewhat longer section along the lower two-thirds of the curve from *B* to *D*, where the molar ratios, CaO/Al_2O_3, of the solid phases are close to 4, but the initial solutions from which these phases precipitated were much more basic than a tetracalcium aluminate solution.

Two explanations may be postulated for the rather gradual increase from 2 to 4 in the molar ratios, CaO/Al_2O_3, of the precipitates resulting as the molar ratios of the initial solutions increase beyond 2.1: (a) That the solubility data pertain to overlapping solubility curves of a series of separate hydrated calcium aluminates of simple molar ratios, which were not at equilibrium at the time of filtering; or (b) that the curve represents the solubility of a solid-solution series of hydrated aluminates varying continuously in molar ratio, CaO/Al_2O_3, from 2 to 4. The fact that these haxagonal phases are metastable makes it impossible to determine which of these explanations is correct, merely from these experiments, where the solid phases were precipitated from supersaturation.

The next step was to approach equilibrium from a state of undersaturation, by placing separately crystalline hydrated dicalcium and tetracalcium aluminates in calcium hydroxide solutions of increasing concentrations. Three series of mixtures were prepared, containing, in each case, 2 g of the hydrated calcium aluminate per liter of solution. In series *A* the dicalcium aluminate, which had been dried over $CaCl_2$, had the molar composition $2.12CaO.Al_2O_3.6.39H_2O$. The dicalcium aluminate of series *B* was not dried over $CaCl_2$, but was used within a few hours after its preparation. It was merely washed with alcohol and ether. This hydrate had the molar composition $2.07CaO.Al_2O_3.8.23H_2O$. Both of these preparations had slightly more lime than theoretically required for dicalcium aluminate. The hydrated tetracalcium aluminate used in the third series, *C*, was somewhat deficient in lime, since its formula computed from the analysis was $3.93CaO.Al_2O_3.11.72H_2O$. This product had been dried over $CaCl_2$ prior to analysis. The individual mixtures of the three series were shaken from time to time and filtered, as before, at the first appearance of a solid phase other than hexagonal aluminates.

Table 2 contains data relative to these solubility experiments. Column 2 gives the concentration of the calcium hydroxide solutions (expressed as grams of CaO per liter) to which the crystalline hydrated calcium aluminates were added.

The manner in which the hydrated aluminates dissolved in the calcium hydroxide solutions of increasing concentrations is shown in figure 2. The points representing the compositions of the resulting solutions fall fairly well along the curve *ABD*, as transferred from figure 1, wherein equilibrium had been approached by precipitation

from the unstable supersaturated aluminate solutions. The numbers accompanying the points refer to the numbers of the experiments of table 2.

The behavior of the two preparations of the hydrated dicalcium aluminates (series *A* and *B*) was notably different from that of the hydrated tetracalcium aluminate (series *C*).

The composition of the solution obtained when the $2.12CaO.Al_2O_3.6.39H_2O$ product was added to water (experiment 1) lies on the $2CaO.Al_2O_3$-composition line, slightly below the point at which the curve ABD intersects this line. This suggests that the hydrated dicalcium aluminate may at first dissolve congruently. But, inasmuch as the $2.12CaO.Al_2O_3.6.39H_2O$ product contained some alumi-

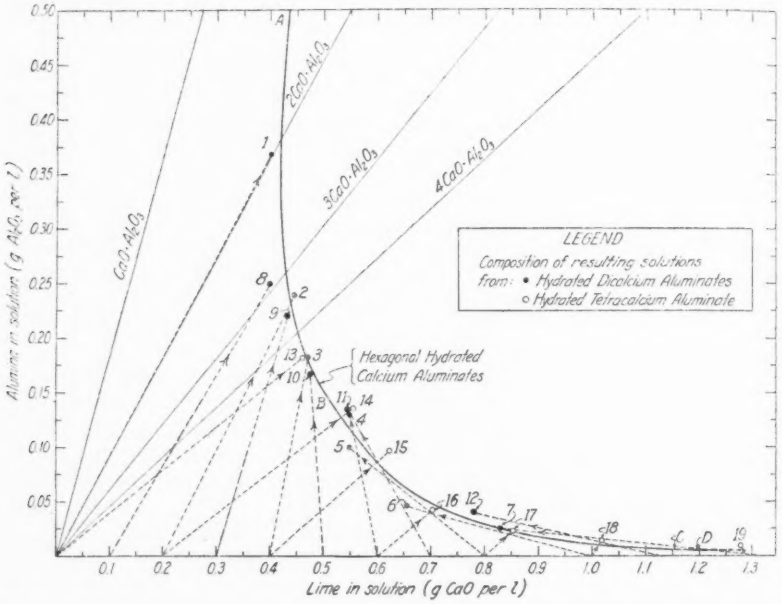

FIGURE 2.—*Composition of the solutions obtained by placing hexagonal hydrated dicalcium and tetracalcium aluminates, respectively, in solutions of calcium hydroxide of increasing concentrations; maintained at a temperature of 21° C.*

nate more basic than dicalcium aluminate, there was an enrichment of the more basic aluminate in the remaining material, evidenced by an increase in molar ratio, CaO/Al_2O_3, of the solid from 2.12 to 2.34. Furthermore, the $2.07CaO.Al_2O_3.8.23H_2O$ preparation, when placed in a solution of calcium hydroxide containing 0.1 g of CaO per liter, appeared to dissolve along a path parallel to the $2CaO.Al_2O_3$—composition line (experiment 8). Likewise, the path of the $2.12CaO.Al_2O_3.6.39H_2O$ preparation was approximately parallel to this line, starting from the point of 0.2 g of CaO per liter (experiment 2). At higher concentrations of calcium hydroxide, lime was removed from solution by both of the preparations of hydrated dicalcium aluminate, and the molar ratio, CaO/Al_2O_3, of the resulting solid phases consequently increased.

TABLE 2.—*Solubility relations pertaining to the hexagonal hydrated calcium aluminates obtained from mixtures of hydrated di- and tetracalcium aluminates, respectively, with calcium hydroxide solutions of increasing concentrations.*

Experiment	Concentration of $Ca(OH)_2$ solutions	Composition of initial mixtures			Time to approach metastable equilibrium [a]	Composition of resulting sloutions			Composition of hexagonal aluminates		
		Al_2O_3	CaO	Molar ratio, CaO/Al_2O_3		Al_2O_3	CaO	Molar ratio, CaO/Al_2O_3	Molar ratio, CaO/Al_2O_3 (calculated)	Molar ratio, CaO/Al_2O_3 (analysis)	Molar ratio, H_2O/Al_2O_3 (analysis)
1	2	3	4	5	6	7	8	9	10	11	12
Series *A*—Dicalcium aluminate (2 g of 2.12 $CaO.Al_2O_3.6.39\ H_2O$ per liter of solution)											
	g of CaO/liter	*g/liter*	*g/liter*		*Days*	*g/liter*	*g/liter*				
1	0	0.607	0.708	2.12	1.3	0.369	0.402	1.98	2.34	2.47	7.40
2	.200	.607	.908	2.72	134	.238	.438	3.34	2.31		
3	.400	.607	1.108	3.32	87	.183	.469	4.66	2.74	2.64	8.72
4	.600	.607	1.308	3.92	55	.131	.549	7.62	2.90	3.03	9.19
5	.800	.607	1.508	4.52	23	.099	.549	10.1	3.43	3.51	10.40
6	1.000	.607	1.708	5.12	23	.046	.654	25.9	3.42	3.63	10.92
7	1.310	.607	2.018	6.04	23	.025	.826	60.0	3.77	3.74	11.67
Series *B*—Dicalcium aluminate (2 g of 2.07 $CaO.Al_2O_3.8.23\ H_2O$ per liter of solution)											
8	0.100	0.557	0.734	2.40	8	0.248	0.397	2.91	1.98	1.87	[b] 8.15
9	.300	.557	.934	3.05	4	.219	.429	2.99	2.72	2.65	[b] 9.81
10	.500	.557	1.134	3.70	3	.166	.474	5.19	3.07	2.96	[b] 10.49
11	.700	.557	1.334	4.35	8	.134	.547	7.42	3.38	3.22	[b] 11.00
12	1.123	.557	1.757	5.71	3	.041	.778	23.9	3.57	3.66	[b] 12.03
Series *C*—Tetracalcium aluminate (2 g of 3.93 $CaO.Al_2O_3.11.72H_2O$ per liter of solution)											
13	0	0.382	0.826	3.93	16	0.182	0.460	4.59	3.33	3.32	10.03
14	.200	.382	1.026	4.88	16	.137	.555	7.36	3.49	3.37	10.41
15	.400	.382	1.226	5.83	16	.097	.623	11.7	3.85	3.78	11.62
16	.600	.382	1.426	6.79	16	.042	.704	30.5	3.86	3.84	12.06
17	.800	.382	1.626	7.74	16	.023	.852	67.2	3.92	3.91	11.95
18	1.000	.382	1.826	8.69	16	.015	1.018	123	4.00	3.87	11.84
19	1.230	.382	2.116	10.1	16	.009	1.279	259	4.08	3.89	11.97

[a] Time which elapsed between preparation of mixtures and subsequent filtration occasioned by appearance of microscopically detectable quantities of solid phases other than metastable hexagonal hydrated calcium aluminates.

[b] Not dried over $CaCl_2$ prior to determining molar ratio, H_2O/Al_2O_3, as in case of series *A* and *C*.

On the other hand, the hydrated tetracalcium aluminate does not appear to dissolve congruently when placed in water (experiment 13), since the composition of the resulting solution does not lie on the $4CaO.Al_2O_3$-composition line. The molar ratio, CaO/Al_2O_3, of the solid material was reduced to 3.33. The hydrated tetracalcium aluminate placed in the calcium hydroxide solution containing 0.2 g of CaO per liter also gave up appreciable lime to the solution in excess of that of the proportion of 4 CaO to 1 Al_2O_3, and, consequently, the molar ratio, CaO/Al_2O_3, of the solid was reduced, this time to 3.49. At the higher concentrations of calcium hydroxide the hydrated tetracalcium aluminate dissolved with little or no change in molar composition.

Summarizing the results of the solubility experiments obtained at this stage, several conclusions can be drawn. The molar ratio, CaO/Al_2O_3, of the solid phases when equilibrium was approached

from undersaturation corresponded fairly well with those obtained along the various segments of the curve ABD where equilibrium had been approached from supersaturation. Thus, solid phases having a molar ratio, CaO/Al_2O_3, of 4, or approximately 4, were obtained at the higher concentrations of lime along ABD not only by an approach to equilibrium from supersaturation (table 1 and fig. 1) but also by two approaches from undersaturation (table 2 and fig. 2), namely, when the hydrated tetracalcium aluminate had been placed in the more concentrated solutions of calcium hydroxide and when the hydrated dicalcium aluminates had removed considerable lime from such solutions. The molar ratio, CaO/Al_2O_3, of the solid material was about 2 only at the lower concentrations of lime, but in this case the hydrated tetracalcium aluminates did not yield such a product. The significance of these solubility experiments will become clearer after consideration has been given to the findings of the X-ray studies.

(b) MOLAR RATIO, H_2O/Al_2O_3, IN THE HEXAGONAL CALCIUM ALUMINATES

One has but to review the literature on the hexegonal hydrated calcium aluminates to realize that there is a difference of opinion as to their exact water content.

The difficulties involved in determining the water content of the plate forms become apparent merely from a consideration of the nature of these crystalline compounds. In the first place, these aluminates are made up of very thin layers of hexagonal (or pseudohexagonal) plates and are highly hydrated. Furthermore, a portion of the water is readily lost even at relatively high humidities [13]. One is always in doubt, therefore, whether the water so lost may have been (1) absorbed water, because thin crystals of this character have such large surfaces, (2) water between the laminas of the crystals, or (3) water of crystallization. The presence of either absorbed water or water between the laminas of the crystals as a possible source of error in the determination of the refractive indices of the plate forms has been pointed out in a previous publication [1] and, more recently, has been mentioned by other investigators. Obviously, the drying of these crystals should have as its objective the removal of the absorbed water and water between the laminas as completely as possible without the loss of any of the water of crystallization. Assarsson [4, 5, 6, 7] washed his samples with a little water, then with alcohol (or acetone), and finally with ether, and omitted further drying prior to analysis. Others have used various methods of drying. As stated previously, the hydrates in the present investigation were, for the most part, washed with alcohol and ether, and then were dried at room temperature in a desiccator containing $CaCl_2$.

This method may be open to criticism (as may also many other methods of drying) in that there is no assurance that some of the water of crystallization may not have been lost. Accordingly, in some instances, which will be mentioned subsequently, the samples were not dried over $CaCl_2$.

The molar ratios, H_2O/Al_2O_3, in the hexagonal hydrated calcium aluminates, as determined from loss on ignition, are given in column 11 of table 1 and column 12 of table 2. It can be seen from these tables that, in general, the molar ratio, H_2O/Al_2O_3, increased with an increase in the molar ratio, CaO/Al_2O_3.

Figure 3 shows the molar ratios, H_2O/Al_2O_3, plotted against the molar ratios, CaO/Al_2O_3, not only for these hexagonal hydrated calcium aluminates dried over $CaCl_2$ (differentiated by closed circles), but also for similar ratios calculated from data of other investigators, including Assarsson [4, 5, 7], Mylius [8], Thorvaldson, Grace, and Vigfusson [9], Koyanagi [10], Salmoni [11], Lafuma [12], Bessey [13], Kühl, Thilo, and Chi Yü [14], Pulfrich and Linck [15], MacIntire and Shaw [16], and Travers and Sehnoutka [17].

The hydrates prepared by Assarsson (open circles) likewise show that an increase in molar ratio, CaO/Al_2O_3, is attended by an increase in molar ratio, H_2O/Al_2O_3. But, almost invariably, his products, which were not dried, contained more water than those dried over $CaCl_2$ in this laboratory.

With few exceptions the points representing the compositions of all of the preparations are contained in a field bounded by the following limits:

$$\begin{array}{ccc} 2CaO.Al_2O_3.9H_2O & \text{——} & 4CaO.Al_2O_3.14H_2O \\ | & & | \\ 2CaO.Al_2O_3.5H_2O & \text{——} & 4CaO.Al_2O_3.12H_2O \end{array}$$

(c) OPTICAL PROPERTIES OF THE HEXAGONAL CALCIUM ALUMINATES

Microscopical examination of samples of the materials from the mixtures of calcium aluminate and calcium hydroxide solutions showed the presence of flat hexagonal plates or spherulites consisting of radiating aggregates of these crystals. Usually the individual plates were so small that satisfactory interference figures could not be obtained to determine whether the crystals were uniaxial or biaxial. Consequently, the refractive indices given in columns 12 and 13 of table 1 are recorded as those of ω and ϵ, respectively.

There are no very marked differences in the refractive indices of these hexagonal hydrated calcium aluminates, especially those of ϵ. The ω indices of the dicalcium aluminates were, however, lower than those of the tetracalcium aluminates. Inasmuch as the refractive indices of certain of these products, differing considerably in chemical composition, are nearly identical, the differentiation of the plate forms by microscopical means was difficult.

Table 3 gives data obtained by various investigators on the plate forms of the hydrated calcium aluminates for which the molar ratios, CaO/Al_2O_3, were fairly close to 2, 3, and 4. The methods of washing and drying the products differed markedly, and the moles of H_2O per mole of $2CaO.Al_2O_3$ and of $3CaO.Al_2O_3$ ranged from 5 to 11.3 and from 7 to 12.5, respectively. Where refractive indices have been reported, the values of ω and ϵ are recorded, and in these cases the optical character has been stated to be uniaxial negative. In most instances, the water content of the dicalcium aluminates listed in table 3 was higher, and the refractive indices were lower than for the dicalcium aluminates given in table 1.

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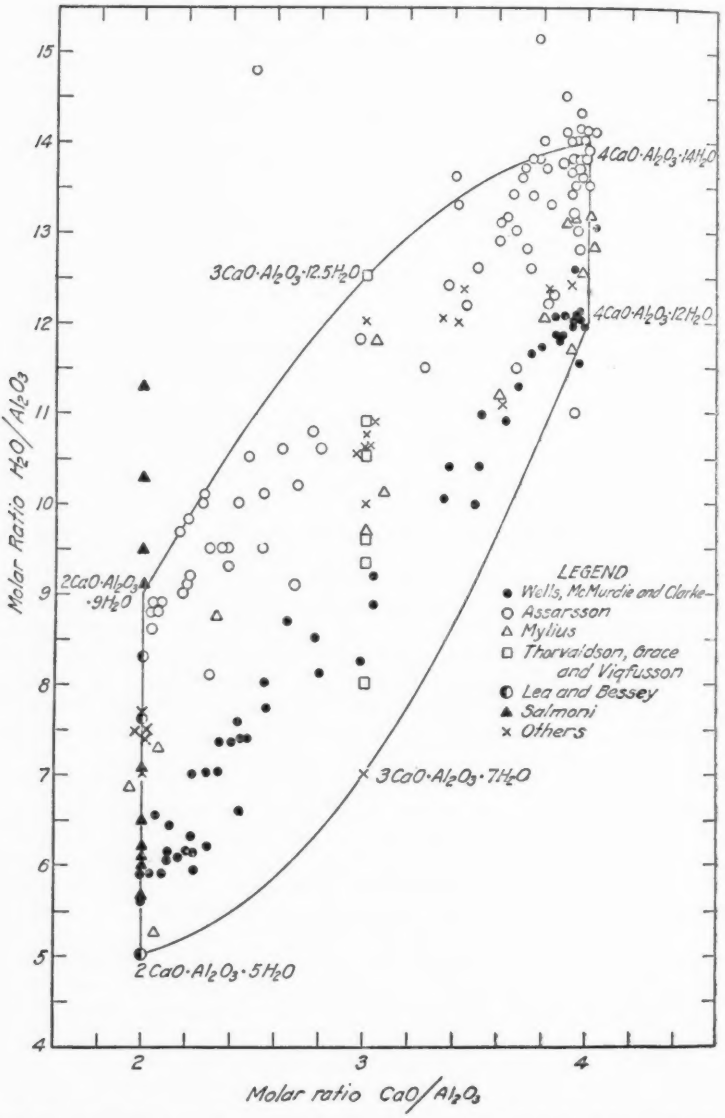

FIGURE 3.—*Composition of preparations of hexagonal hydrated calcium aluminates obtained by various investigators.*

TABLE 3.—*Water content and optical properties of hydrated calcium aluminates (plate forms) as given by various investigators*

TABLE 3.—*Water content and optical properties of hydrated calcium aluminates (plate forms) as given by various investigators.*

Moles of H_2O	Refractive Indices		Optical character	Observers	Method of preparation	Method of drying
	ω[a]	ϵ[a]				
				$2CaO.Al_2O_3.XH_2O$		
7.0				Allen and Rogers [22] (1909)	Al-metal+solution $Ca(OH)_2$	Over $CaCl_2$.
7.0				Lafuma [12] (1925)	Partial hydrolysis $4CaO.Al_2O_3.12H_2O$ in water.	Do.
8.2				Koyanagi [23] (1930)	Precipitation from calcium aluminate solution.	Not stated.
8.4	1.519	1.506	Uniaxial negative	Assarsson [5] (1931)	Calcium aluminate solution+$Ca(OH)_2$ solution.	Washed with alcohol and ether. Drying not stated.
7.6	1.520	1.512	do	Koyanagi [10] (1932)	Calcium aluminate cement+$Ca(OH)_2$ solution.	Not stated.
6.8	1.522	1.502	do	Mylius [8] (1933)	Hydrated alumina gel+$Ca(OH)_2$ solution.	Washed with water, dried 24 hr. in vacuum over $CaCl_2$.
7.3	1.522	1.502	do	do	Potassium aluminate solution+$Ca(OH)_2$ solution.	Washed with water and ether, dried 24 hr. in vacuum over $CaCl_2$.
5.3				do	do	In vacuum over P_2O_5.
8.7				Salmoni [11] (1934)	Direct hydration at 0° C of a clinker of the composition $2CaO.Al_2O_3$.	Washed with water, alcohol or acetone, and ether at 0° C.
7.1				do	do	Over $CaCl_2$ for 24 hr.
5.7				do	do	Over P_2O_5 at 20° C.
6.5				do	do	Over $CaCl_2$ at 20° C.
6.0				do	do	Over H_2SO_4, 76 percent, at 20° C.
6.1				do	do	Over H_2SO_4, 72 percent, at 20° C.
6.2				do	do	Over H_2SO_4, 63 percent, at 20° C.
9.1				do	do	Saturated solution of Na_2SO_4 at 20° C.
9.5				do	do	Saturated solution of KCl at 20° C.
10.3				do	do	Saturated solution of $Pb(NO_3)_2$ at 20° C.
11.3				do	do	Saturated solution of KIO_3 at 20° C.
8.7	1.519	1.506	Uniaxial negative	Assarsson [7] (1936)	Precipitation from calcium aluminate solution.	Washed with alcohol and ether, drying not stated.
9.0	1.519	1.506	do	do	Salmoni's method	Do.
9.0	1.523	1.510	do	Nacken [24] (1937)	Not stated	Not stated.
8.3	1.520	1.505	do	Bessey [13] (1938)	Not stated	At vapor pressure equivalent to 13.5 mm Hg at 17° C.
7.6	1.521	1.512	do	do	do	At vapor pressure equivalent to 2.8 mm Hg at 17° C.
5.0	1.540	1.530	do	do	do	Over CaO at 17° C.

See footnote at end of table.

TABLE 3.—*Water content and optical properties of hydrated calcium aluminates (plate forms) as given by various investigators*—Continued

Moles of H_2O	Refractive Indices		Optical character	Observers	Method of preparation	Method of drying
	ω^a	ϵ^a				
				$3CaO.Al_2O_3.XH_2O$		
12.0				Candlot [18] (1890)	Direct hydration $3CaO.Al_2O_3$	
10.0				Gallo [20] (1908)	Calcium aluminate solution $Ca(OH)_2$ solution.	Between sheets of filter paper.
	1.520	1.504	Uniaxial negative	Klein and Phillips [19] (1914)	Direct hydration $3CaO.Al_2O_3$	Not stated.
10.5				do	do	Over concentrated H_2SO_4, 24 hr.
9.0				do	do	Over concentrated H_2SSO_4, 48 hr. in vacuum.
7.0	1.538	1.523	Uniaxial negative	Pulfrich and Linck [15] (1924)	do	In air at room temperature.
10.0				MacIntire and Shaw [16] (1925)	Hydrated alumina gel+$Ca(OH)_2$ solution.	Do.
12.5	1.527	1.505	Uniaxial negative	Thorvaldson, Grace, and Vigfusson [9] (1929).	Direct hydration $3CaO.Al_2O_3$ in cold	Over saturated solution of $Pb(NO_3)_2$ (18.1 mm Hg).
10.9	1.530	1.510	do	do	do	Over saturated solution of KCl (16.1 mm Hg).
8.0	1.538	1.520	do	do	do	Over CaO to constant weight.
12.5	1.529	1.505	do	Assarsson [5] (1931)	Calcium aluminate solution+$Ca(OH)_2$ solution.	Washed, alcohol (or actone) and ether. Drying not stated.
10.7	1.539	1.524	do	Koyanagi [21] (1931)	do	Washed, alcohol and ether, dried in vacuum desiccator.
11.8	1.528	1.508	do	Mylius [8] (1933)	Potassium aluminate solution+$Ca(OH)_2$ in excess KOH.	Washed, alcohol and ether, dried 2 hr. with vacuum, 24 hr. without vacuum over $CaCl_2$.
10.1				do	Potassium aluminate solution+$Ca(OH)_2$ solution.	Washed with water, alcohol, and ether and dried to constant weight over $CaCl_2$.
9.7				do	do	Over P_2O_5, without vacuum, 71 days.

$4CaO.Al_2O_3.XH_2O$

12				Le Chatelier [25] (1887)	Calcium aluminate solution+$Ca(OH)_2$ solution.	Not stated.
12				Lafuma [12] (1925)	Calcium aluminate solution+$Ca(OH)_2$	Over NaCl.
12.0	1.532	1.505	Uniaxial negative	Wells [1] (1928)	Calcium aluminate solution+saturated $Ca(OH)_2$ solution.	Over $CaCl_2$.[a]
12.+	1.533	1.514	Optically negative	Assarsson [4] (1930)	Al metal+saturated $Ca(OH)_2$ solution	Washed with alcohol and ether. Drying not stated.
13.5	(γ)1.538	(α)1.510	Biaxial negative ($2V=14°$)	Assarsson [5] (1931)	Calcium aluminate solution+saturated $Ca(OH)_2$ solution.	Do.
13.0	1.533	1.522	Uniaxial negative	Mylius [8] (1933)	Potassium aluminate solution+$Ca(OH)_2$ solution.	Washed alcohol and ether. Dried in air.
12.0	1.549	1.533	do	do	By drying 13.0 hydrate over $CaCl_2$	Over $CaCl_2$ in vacuum.
14.0	(γ)1.535	(α)1.520	Biaxial negative (alpha form) $2V=10°$.	Assarsson [7] (1936)	Calcium aluminate solution+$Ca(OH)_2$ solution.	Washed alcohol and ether. Drying not stated.
14.0	(γ)1.535	(α)1.507	Biaxial negative (beta form) $2V=14°$.	do	do	Do.
12.0	(γ)1.549	(α)1.527	Biaxial negative (dehydrated alpha).	do	By dehydrating the alpha form (14.0 hydrate).	Do.
12.0	(γ)1.542 (β)1.538	(α)1.522	Biaxial negative $2V$ (calculated from $2E$)=38°. $2V$(calculated from indices)=25°.	Wells, Clarke, and McMurdie	Calcium aluminate solution+CaO	Over $CaCl_2$.
12.0	(γ)1.557 (β)1.553	(α)1.535	Biaxial negative $2V$ (calculated from $2E$)=24°±2°.	Tilley, Megaw, and Hay [26] (1934)	Hydrocalumite, a mineral from Scawt Hill, Co. Antrim, Ireland.	

[a] In those cases in which the crystals are biaxial negative, the indices of refraction are differentiated parenthetically as (γ) and (α) instead of ω and ϵ, respectively, which pertain to the uniaxial crystals. In two instances the β index is also included.

The water content of the hydrated tetracalcium aluminates has been reported as varying only from about 12 to 14H_2O. Furthermore, the optical character of these aluminates had been given variously as uniaxial and biaxial negative.[3] In addition to those of other investigators, data are given in table 3 for a biaxial form [4] which has been prepared in this laboratory. The properties of the mineral hydrocalumite are also included.

The refractive indices of all of the artificially prepared tetracalcium aluminate hydrates having 12.0 moles of H_2O are lower than those of the mineral hydrocalumite found in altered intrusive contact-rocks in Ireland and described by Tilley, Megaw, and Hey [26]. Bessey [13] suggests that the high refractive indices may be explained on the basis that the mineral contained 1.8 percent of carbon dioxide, probably held in solid solution, since he prepared a tetracalcium carbonato-aluminate of the formula

$$4CaO.Al_2O_3.CO_2.11H_2O \text{ (or } 3CaO.Al_2O_3.CaCO_3.11H_2O),$$

which had indices of refraction of $\omega=1.552 \pm 0.003$ and $\epsilon=1.532 \pm 0.003$. He is of the opinion that a small amount of this compound, by this solid-solution formation, may influence the structure of the tetracalcium aluminate hydrate and thus have a bearing on the indices observed by others. Bessey does not state whether the carbonato-aluminate is uniaxial or biaxial in optical character.

(d) X-RAY DIFFRACTION PATTERNS OF THE HEXAGONAL CALCIUM ALUMINATES

In order to study further the relationships of the various hexagonal forms of the hydrated calcium aluminates, X-ray powder patterns were made by means of copper radiation. The cylindrical cameras had a radius of about 52 cm. The radiation was filtered with nickel foil, and the camera radius was calibrated with NaCl.

Patterns were first made on eight freshly prepared samples, whose compositions ranged from about $2CaO.Al_2O_3.8H_2O$ to about $4CaO.Al_2O_3.13H_2O$,[5] as shown in table 4.

The indexed interplanar spacings and relative intensities of the lines of sample 1 ($2.O4CaO.Al_2O_3.7.92H_2O$) are given in table 5. The lines appear to be those of a compound having an hexagonal unit cell in which $a=8.8$ A and $c=10.6$ A.

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[3] In those cases in which the crystals are biaxial negative, the indices of refraction are differentiated parenthetically in table 3 as (γ) and (α) instead of ω and ϵ, respectively, which pertain to the uniaxial crystals. In two instances the β index is also included.

[4] This particular preparation of tetracalcium aluminate hydrate was obtained by adding to a highly supersaturated monocalcium aluminate solution a quantity of freshly ignited CaO in excess of that required to combine with the alumina for the formation of a tetracalcium aluminate, and, in addition, to somewhat more than saturate the solution with regard to $Ca(OH)_2$. The resulting $Ca(OH)_2$ formed as a solid phase was then dissolved by replacing portions of the saturated solution of the mixture by water until the concentration of calcium hydroxide in solution was decreased to a value slightly under that at saturation. The crystals of the aluminate were then allowed to develop for slightly over 3 years. After filtering, the crystals were washed with alcohol and ether and dried in a desiccator containing $CaCl_2$. Analysis of this preparation gave the composition 41.3 percent of CaO, 19.1 percent of Al_2O_3, 39.6 percent of H_2O, corresponding to the ratios: $3.93CaO:1.00Al_2O_3:11.72H_2O$. Microscopical examination revealed the presence of a few percent of the isometric tricalcium aluminate, $3CaO.Al_2O_3.6H_2O$, as well-formed rhombic dodecahedrons. From subsequent discussion it will become evident why it is difficult to grow well-formed crystals of the hexagonal forms free of the isometric modification. Optical examination by H. Insley, National Bureau of Standards, of this hydrated tetracalcium aluminate showed the presence of platy crystals of hexagonal outline, with the acute bisectrix perpendicular to the plane of the plates. The indices of refraction (with indices of the reference liquids checked on the refractometer at the time of measuring) were: $\gamma=1.542\pm0.003$, $\beta=1.538\pm0.003$, and $\alpha=1.522+0.003$; $2E$ (measured) was $60°\pm5°$; with $2V$ (calculated from $2E$) $=38°$ and $2V$ (calculated from indices) $=25°$.

[5] The indices of refraction of the products having compositions close to $2CaO.Al_2O_3.8H_2O$ were: $\omega=1.519 \pm0.003$, $\epsilon=1.509\pm0.003$; values agreeing fairly well with those reported by other investigators and listed in table 3. Satisfactory optical properties were not obtained with the other freshly prepared samples, given in table 4, because they were very finely divided.

TABLE 4.—*Composition of freshly prepared samples of hexagonal hydrated calcium aluminates, before and after drying over* $CaCl_2$

Experiment	Molar ratio, CaO/Al_2O_3	Molar ratio, H_2O/Al_2O_3 (freshly prepared)	Molar ratio, H_2O/Al_2O_3 (after drying)
1	2.04	7.92	5.85
2	2.11	7.96	5.41
3	2.16	8.10	----
4	2.30	8.44	6.12
5	2.40	9.05	7.92
6	3.15	10.91	9.09
7	3.73	13.68	11.60
8	3.88	12.60	11.23

TABLE 5.—*Interplanar spacings and estimated relative intensities of hexagonal* $2CaO.Al_2O_3.8H_2O$

[*VS*, very strong; *M*, medium; *S*, strong; *W*, weak]

hkl	*d*	Estimated Intensity	*hkl*	*d*	Estimated Intensity
001	10.6	*VS*	310	2.11	*W*
002	5.3	*S*	214	1.955	*W*
201	3.55	*M*	304	1.835	*W*
120	2.87	*S*	410	1.667	*M*
004	2.69	*W*	412	1.591	*W*
122	2.54	*W*	420	1.443	*M*
301	2.48	*M*			

In table 6 are similar data for example 8, of a composition near $4CaO.Al_2O_3.13H_2O$. Here the lines appear to result from an hexagonal cell in which $a=8.8$ *A* and $c=8.2$A. In these two compounds ($2CaO.Al_2O_3.8H_2O$ and $4CaO.Al_2O_3.13H_2O$) the length of the *a* axis is very nearly the same.

In both samples the strong intensities of the 001 lines and the plate habit lead to the probability that the hexagonal calcium aluminates are built up of hexagonal $Ca(OH)_2$ and $Al(OH)_3$ layers with H_2O between them, as suggested by Brandenberger [27].

If, for the purpose of discussion, the formulas are written in the form of hydroxides, $2CaO.Al_2O_3.8H_2O$ becomes $2Ca(OH)_2.2Al(OH)_3.3H_2O$, whereas $4CaO.Al_2O_3.13H_2O$ becomes $4Ca(OH)_2.2Al(OH)_3.6H_2O$. Dividing this last formula by two, it becomes $2Ca(OH)_2.Al(OH)_3.3H_2O$. The densities of the compounds in this series have been reported as ranging from about 2.0 to 2.1 [9, 13]. These densities and the unit-cell sizes would give two "molecules" to a unit cell. Thus, for the dicalcium aluminate hydrate, the cell content is $4Ca(OH)_2.4Al(OH)_3.6H_2O$, and for the tetracalcium aluminate hydrate, the cell content is $4Ca(OH)_2.2Al(OH)_3.6H_2O$. It is evident, therefore, that the difference between the content of one unit cell and the other is $2Al(OH)_3$, and, since the difference in length of the two cells is 2.4 A, it may be assumed that one layer (containing $2Al(OH)_3$) has the thickness of 2.4 A.

The X-ray powder patterns of the samples with compositions intermediate between the above compounds gave lines of both cells. The relative intensities of the 001 lines (at 10.6 and 8.2 A) were in the proper relation to the compositions to indicate the presence, in all cases, of appropriate proportions of the two compounds—$2CaO.Al_2O_3$.

$8H_2O$ and $4CaO.Al_2O_3.13H_2O$. Thus, sample 6, of table 4, with a molar ratio, CaO/Al_2O_3, of 3.15 gave a pattern in which the two 001 lines were of almost equal intensity. Consequently, it appears that the so-called hexagonal tricalcium aluminate hydrate, which has been assumed to be a definite compound by many investigators, is in reality not a separate compound but a mixture of the hexagonal hydrated dicalcium and tetracalcium aluminates in equal molecular proportions.

TABLE 6.—*Interplanar spacings and estimated relative intensities of hexagonal* $4CaO.Al_2O_3.13H_2O$

[*VS*, very strong; *VW*, very weak; *M*, medium; *W*, weak]

hkl	*d*	Estimated intensity	*hkl*	*d*	Estimated intensity
001	8.2	*VS*	004	2.06	*W*
002	4.1	*M*	104	2.000	*W*
111	3.9	*M*	222	1.951	*VW*
210	2.9	*M*	320	1.766	*W*
211	2.73	*W*	410	1.670	*M*
103	2.64	*VW*	411	1.637	*W*
300	2.55	*VW*	403	1.554	*VW*
301	2.45	*M*	501	1.500	*VW*
212	2.37	*W*	323	1.475	*VW*
113	2.31	*VW*	420	1.440	*W*
203	2.24	*M*			

It should be recalled that the hexagonal hydrated calcium aluminates, as a group, exhibit a similarity in optical properties. The indices of refraction of the various samples, in general, increased as the molar ratio, CaO/Al_2O_3, increased. Despite the fact that the X-ray patterns indicate the presence of two crystalline compounds in cases in which the molar ratio, CaO/Al_2O_3, is intermediate between 2 and 4, nevertheless, the products appeared microscopically to consist of only one compound. It is believed, therefore, that the hydrated dicalcium and tetracalcium aluminates, being of very similar structure parallel to the *a* axis, can intercrystallize and give masses which are made up of layers of the one compound so intimately mixed with layers of the other that the average indices of refraction are obtained.

It has been remarked in the literature that all these hexagonal hydrated calcium aluminates have a "family resemblance" in respect to their X-ray powder patterns. In most cases the methods used for obtaining the patterns were such that they did not record lines of interplanar spacings greater than 3 A. Since the lines with large spacings were not obtained, the strongest lines appearing were *hko* lines, and, since the spacings of such lines are functions only of the length of the *a* axis, they are in the same position in the dicalcium and tetracalcium aluminates and mixtures thereof.

A second series of patterns was made on samples of hydrated calcium aluminates of molar ratios of lime to alumina almost identical with those reported above. In this case, however, the samples had been stored in stoppered vials for 2 to 3 years. The losses on ignition of the samples were practically unchanged from those obtained when freshly prepared, but the indices of refraction had increased, especially for those products of low molar ratios of lime to alumina. After storage, the materials all had indices of refraction typical of hydrated tetracalcium aluminate, and the X-ray diffraction patterns, in all cases, were those of hexagonal tetracalcium aluminate hydrate.

Therefore, on standing, $2CaO.Al_2O_3.8H_2O$ breaks down according to the equation:

$$2Ca(OH)_2.2Al(OH)_3.3H_2O \rightarrow 2Ca(OH)_2.Al(OH)_3.3H_2O + Al(OH)_3.$$

Thus, the one extra layer of $Al(OH)_3$ separates out of the crystal, and, since no extra lines are present in the pattern, the $Al(OH)_3$ may be assumed to be amorphous.

A portion of each of the eight samples that had been examined when freshly prepared (table 4) were stored in open dishes over $CaCl_2$ in a desiccator for 3 weeks, and the losses on ignition were then redetermined. The water content in the $2CaO.Al_2O_3.8H_2O$ compound had dropped to about 6 moles. In the composition $4CaO.Al_2O_3.13H_2O$ the content of H_2O after dry storage was 11.23 moles. Preparations of intermediate compositions had lost water proportionately.

X-ray diffraction patterns were made on these dried samples. The sample with composition $4CaO.Al_2O_3.11.23H_2O$ had a pattern very similar to that of the freshly prepared compound with about 13 moles of H_2O. There was, however, a slight but definite decrease in the size of the unit cell along the *c* axis. The dried material had a *c* axis of about 8.1 A in length. All samples of lower molar ratios, CaO/Al_2O_3, had broken down almost completely to the tetracalcium aluminate hydrate, just as had those stored for several years, in closed vials.

Although the X-ray diffraction patterns showed that the dicalcium aluminate hydrate dissociated into the tetracalcium aluminate hydrate and amorphous hydrated alumina on storage in the dry state, it is not known from this investigation whether this conversion occurs in contact with the calcium aluminate solutions. Bessey states, in his discussion of an article by Büssem [28], that $2CaO.Al_2O_3.8H_2O$ in contact with its saturated solution in water is converted to the tetracalcium compound without recrystallization or change in crystal form, but with liberation of hydrated alumina. He also states that, in contact with solutions of higher lime concentration, the dicalcium aluminate hydrate is converted to the similar tricalcium or tetracalcium compound, again without disturbance of the existing crystals. Bessey, however, does not give the direct experimental evidence on which he based his assertions. The X-ray data of the present investigation have shown no evidence for the existence of a hexagonal hydrated tricalcium aluminate. The conversion of the dicalcium aluminate into the tetracalcium aluminate when kept in contact with solutions of higher lime concentrations, is, however, confirmed.

The relation of these compounds to the natural mineral hydrocalumite ($4CaO.Al_2O_3.12H_2O$) [26] is not clear. This mineral is monoclinic and appears to be made up-of alternate layers, just as seems to be the case in these hexagonal compounds. The cell characteristics $a=9.6$ A, $b=11.4$ A, $c=16.84$ A, $\beta=69°$ are not similar to the hexagonal compounds considered here.

(c) DISCUSSION OF THE HEXAGONAL CALCIUM ALUMINATES

From the X-ray studies of the relations of the hexagonal hydrated calcium aluminates, it is now evident that of the two explanations formerly postulated for the more or less gradual increase in the molar ratio, CaO/Al_2O_3, in the aluminates along the curve *ABD* of figure 1,

the first, namely, that the solubility data pertain to overlapping solubility curves of separate hydrated aluminates ($2CaO.Al_2O_3.8H_2O$ and $4CaO.Al_2O_3.13H_2O$), is more valid than the second—that involving a solid-solution series. If this "curve" is now reexamined, it will be noted that there is a limited section where the molar ratio, CaO/Al_2O_3, is perhaps close enough to 2 to warrant the conclusion that this applies primarily to the dicalcium aluminate hydrate. Likewise, at the higher lime concentrations there is a section which might be ascribed as pertaining mainly to the solubility of the hexagonal tetracalcium aluminate hydrate. The portion between these two sections may logically correspond to that region where the two aluminates markedly intercrystallize because of the close similarity of their crystal structures. That no evidence of the existence of a hexagonal hydrated tricalcium aluminate was obtained in this study lends weight to this argument.

If these explanations are correct, there should be a metastable invariant point (since both hexagonal aluminates, as will be shown later, are metastable with regard to the isometric aluminate $3CaO.Al_2O_3.6H_2O$) where the solution is saturated with respect to both the dicalcium and tetracalcium aluminates. But, in view of the extreme difficulty in obtaining equilibrum, it may not be found possible to trace the metastable curves individually with sufficient accuracy to establish this point. Notwithstanding, it is believed that the metastable invariant point, $2CaO.Al_2O_3.8H_2O$, $4CaO.Al_2O_3.13H_2O$, and solution, lies somewhere between 0.5 and 0.6 g of CaO and 0.10 and 0.15 g of Al_2O_3 per liter. At concentrations of lime greater than that at the invariant point, the solutions in metastable equilibrium with dicalcium aluminate appear to be supersaturated with respect to the tetracalcium aluminate, and, consequently, the mixture is predominantly composed of the tetracalcium aluminate, whereas at the lower concentrations of lime the reverse seems to hold. There should also be a second metastable invariant point for $4CaO.Al_2O_3.13H_2O$, $Ca(OH)_2$, and a solution containing about 1.15 g of CaO per liter and somewhere between 0.005 and 0.01 g of Al_2O_3 per liter.

The point of intersection of the curve *AED* with the $2CaO.Al_2O_3$-composition line gives a value slightly higher than that suggested by Bessey [13] for the solubility of $2CaO.Al_2O_3.8H_2O$, as well as that found in this study where equilibrium was approached from undersaturation.

The relation of the biaxial form (or forms) of the tetracalcium aluminate to the uniaxial hexaginal modification in the system $CaO\text{-}Al_2O_3\text{-}H_2O$ at 21° C warrants further study.

2. TRANSITION OF THE HEXAGONAL HYDRATED CALCIUM ALUMINATES INTO THE ISOMETRIC TRICALCIUM ALUMINATE HEXAHYDRATE, $3CaO.Al_2O_3.6H_2O$, IN THE SYSTEM AT 21° C

Attention will now be directed to the changes which took place when the mixtures of calcium aluminate-calcium hydroxide solutions were not filtered at the first appearance of phases other than the metastable hexagonal hydrated calcium aluminates. The first of these changes to be considered will be the transition of the hexagonal forms into the isometric tricalcium aluminate hexahydrate, $3CaO.Al_2O_3.6H_2O$. This crystalline hydrated aluminate can be recognized

readily with a microscope by its refractive index, which is close to 1.605. Well-formed icositetrahedrons or rhombic dodecahedrons having this index were observed in 1928 by one of the present authors in a previous study of the reaction of water on the calcium aluminates [1]. However, as the crystals were associated with other phases, they were not recognized as being the compound $3CaO.Al_2O_3.6H_2O$ that had been noted by Allen and Rogers [22] as early as 1900. After the careful investigation of Thorvaldson and Grace [29], there was no doubt concerning the identity of the crystals previously observed.

By following the changes in the crystalline phases, it was noticed that the isometric crystals grew at the expense of the hexagonal forms. After appreciable quantities of the isometric crystals had been formed, several of the mixtures were filtered, and the solid phases and resulting solutions were analyzed to ascertain the region in the diagram where the changes were taking place.

Figure 4 shows this region, together with the curve *ABD* (pertaining to the hexagonal hydrated aluminates) which has been transferred from figure 1. The closed circles give the compositions of the initial unstable calcium aluminate solutions, and the open circles containing crosses, the compositions of the resulting solutions following partial transformation of the hexagonal phases into the isometric $3CaO.Al_2O_3.6H_2O$. Although the numbers accompanying the lines connecting these points give the molar ratios, CaO/Al_2O_3, in the solid phases thus formed, the connecting lines do not reveal the actual paths of precipitation except in those instances in which these ratios remain as 3. Thus, it can be seen from figure 1 that for the hexagonal aluminates this ratio was approximately 3 along that section of the curve *ABD* where the concentration of lime ranged from about 0.5 to about 0.6 g CaO per liter. From figure 4, it is apparent that, as the formation of the isometric aluminate carried the precipitation beyond that section of the curve *ABD*, the precipitation continued along paths closely parallel to the $3CaO.Al_2O_3$-composition line.

The molar ratio, CaO/Al_2O_3, of the hexagonal aluminates was less than 3 along that section of the curve *ABD* of figure 1 where the concentration of lime was less than 0.5 g of CaO per liter. As the isometric was formed in this region, this molar ratio of the solid phases increased to about 3 (fig. 4). Such an increase could take place only by a removal of lime from solution. This, coupled with the fact that the hexagonal phases are metastable with respect to the isometric phase, resulted in the solutions moving away from the curve *ABD*, but at slopes different from those of the connecting lines of figure 1.

On the other hand, the conversion of the hexagonal aluminates having molar ratios greater than 3 (at lime concentrations greater than 0.6 g of CaO per liter along *ABD* of fig. 1) into the isometric $3CaO.Al_2O_3.6H_2O$ must, at first, have liberated lime to the solutions. But, since the solubility of the hexagonal aluminates decreases in this region as the concentration of lime in solution increases, the tendency would be for the solutions to change in composition along this section of the curve *ABD*. Figure 4 shows that in three instances (those wherein the molar ration, CaO/Al_2O_3, of the solid phases were 3.24, 3.34, and 3.58) the compositions did remain on this curve. In four other instances, where the conversion of the hexagonal aluminate to the isometric was more complete, the continued formation of the more

stable $3CaO.Al_2O_3.6H_2O$ eventually carried the precipitation beyond the curve *ABD*.

Because appreciable quantities of the hexagonal forms of the hydrated calcium aluminates still persisted in the solid phase of the reaction mixtures which had been filtered, the remaining unfiltered mixtures were set aside to permit the further transformation into the isometric modification to proceed more nearly to completion. The object in view was to construct a solubility curve for the isometric hydrate. In the meantime, a considerable quantity of $3CaO.Al_2O_3.6H_2O$ was prepared and placed in calcium hydroxide solutions of increas-

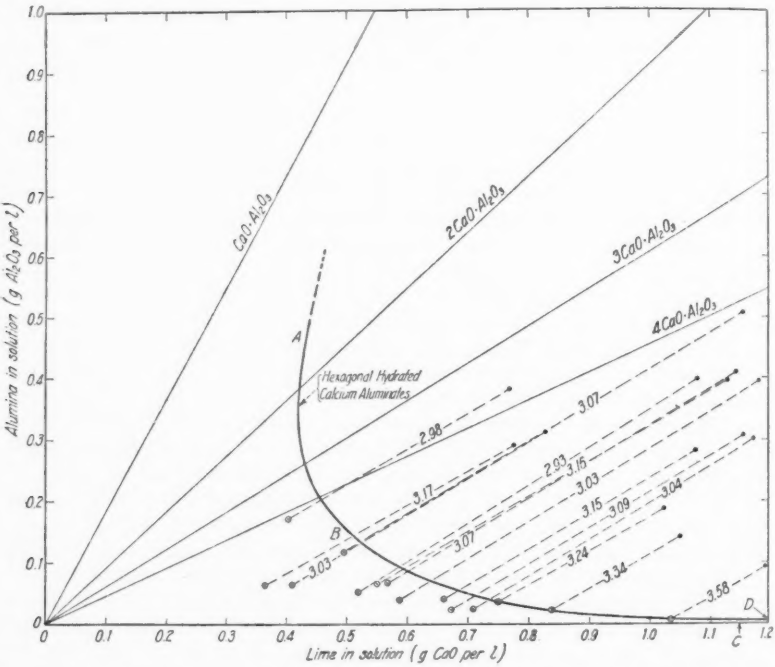

FIGURE 4.—*Composition of the calcium aluminate solutions resulting from partial transformation of the metastable hexagonal hydrated calcium aluminates into the stable isometric tricalcium aluminate hexahydrate* $3CaO.Al_2O_3.6H_2O$ *at 21° C.*

ing concentrations to approach equilibria in this manner. Consideration will now be given to the results of these experiments.

3. ISOMETRIC TRICALCIUM ALUMINATE HEXAHYDRATE, $3CaO.Al_2O_3.6H_2O$, IN THE SYSTEM AT 21° C.

The isometric hexahydrate $3CaO.Al_2O_3.6H_2O$ was prepared, in a platinum dish, by direct hydration of anhydrous tricalcium aluminate with saturated steam at 177° C (equivalent to a pressure of 150 lb/in.^{2}) following the general procedure described by Thorvaldson and Grace [29]. Despite the fact that the preparation was steamed twice, it still contained a small quantity of the hexagonal phase, estimated microscopically to be 1 percent or less. The index of refraction of the isometric hydrate was very close to 1.605.

Two series of reaction mixtures that contained, in each instance, 1 g of the isometric hydrate per liter of a clear solution of calcium hydroxide were then prepared. The concentration of the calcium hydroxide solutions ranged from the equivalent of 0.0 to 1.296 g of CaO per liter. The mixtures, which were placed in tightly stoppered flasks, were shaken from time to time to facilitate approach to equilibrium. One series was maintained continuously at a temperature of 21° C, and the second was first heated on a steam bath for several hours and then slowly cooled for several hours to the same constant temperature. At intervals of 1 to 3 months, depending upon the changes occuring, aliquots of the filtrates from separate reaction

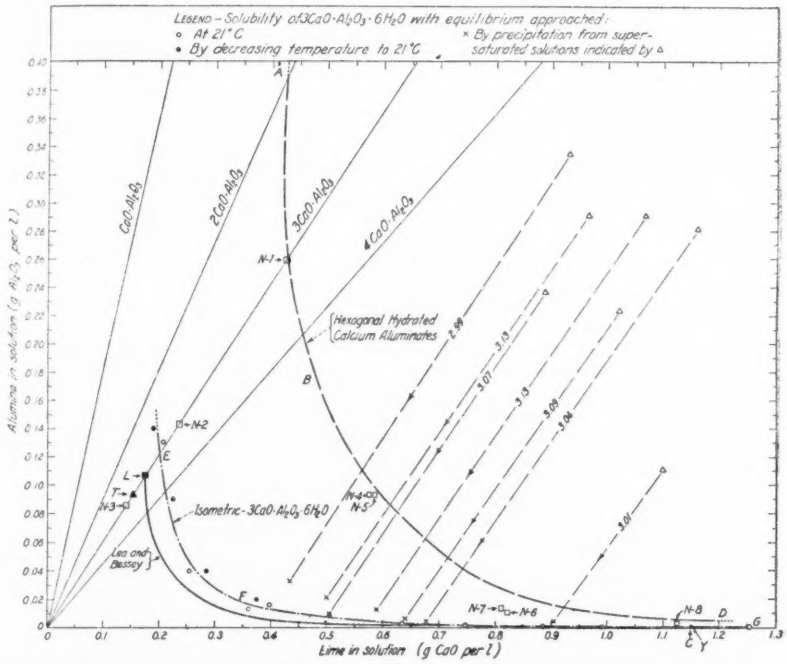

FIGURE 5.—*Solubility relationships of isometric tricalcium aluminate hexahydrate,* $3CaO.Al_2O_3.6H_2O$, *in the system* CaO-Al_2O_3-H_2O *at 21° C.*

mixtures were taken, until successive analyses indicated that equilibrium had been attained, as evidenced by no successive change in the concentration of dissolved alumina or lime greater than that which could be ascribed to the limits of the accuracy of the analytical procedure.

Data pertaining to these solubility determinations are given in table 7. In figure 5 the quantity of alumina in solution is plotted against the lime in solution, and a curve, EFG, is drawn through these points. The open circles pertain to the solubility values obtained at a constant temperature of 21° C, and the closed circles to those where equilibrium was approached from a higher temperature. The figure also shows a portion of the curve ABD representing the solubility of the hexagonal hydrated calcium aluminates, as transferred from

figure 1. In addition, there are shown seven instances (indicated by crosses) where the solubility curve of $3CaO.Al_2O_3.6H_2O$ was approached from supersaturation. Although the inversions of the hexagonal forms into the isometric had proceeded further than in the examples shown in figure 4, nevertheless, they were still incomplete in several instances, despite the fact that these particular mixtures had stood for over a year.

TABLE 7.—*Solubility of isometric tricalcium aluminate hexahydrate, $3CaO.Al_2O_3.6H_2O$, at 21° C*

[Obtained from mixtures containing 1 g of $3CaO.Al_2O_3.6H_2O$ per liter of both water and aqueous solutions of calcium hydroxide]

Experiment	Composition of calcium hydroxide solutions	Composition of final solutions		Time to approach equilibrium	Equilibrium approached
		Al_2O_3	CaO		
	g of CaO/liter	*g/liter*	*g/liter*	*Days*	
1	0	0.140	0.190	236	Decreasing temperature to 21° C.
2	0	.131	.208	516	At 21° C continuously.
3	.100	.090	.223	108	Decreasing temperature to 21° C.
4	.200	.040	.255	509	At 21° C continuously.
5	.259	.040	.285	260	Decreasing temperature to 21° C.
6	.350	.013	.361	509	At 21° C continuously.
7	.389	.020	.375	478	Decreasing temperature to 21° C.
8	.400	.017	.398	89	At 21° C continuously.
9	.518	.009	.504	89	Do.
10	.648	.002	.632	89	Do.
11	.758	.001	.747	89	Do.
12	.907	.001	.884	89	Do.
13	1.037	.0008	.990	89	Do.
14	1.296	.0003	1.256	89	Do.

Lea and Bessey have determined the solubility of $3CaO.Al_2O_3.6H_2O$ in calcium hydroxide solutions of increasing concentration at a temperature of 25° C, and their curve, as presented by Bessey [13], is reproduced in part in figure 5. It is not extended beyond the concentration of 0.7 g of CaO per liter, since it apparantly coincides at the higher concentrations of lime with the curve obtained in this study. At concentrations less than 0.7 g of CaO per liter, it deviates somewhat from the latter, indicating lower solubilities. The curve as originally drawn by Lea and Desch [30] has not been transferred to figure 5, but it lies between the two curves shown.

The point designated by the letter *L* on the $3CaO.Al_2O_3$-composition line locates the solubility of the compound $3CaO.Al_2O_3.6H_2O$ as given by Bessey, as well as the ascribed invariant point $3CaO.Al_2O_3.6H_2O$-Al_2O_3.aq.

Small quantities of an additional phase (very likely hydrated alumina) were found in the mixtures which had less than 0.3 g of CaO per liter (table 7, experiments 1 to 5, inclusive). The mean refractive index ranged from about 1.56 to 1.58, which is distinctly less than 1.605, the index of $3CaO.Al_2O_3.6H_2O$. At concentrations of lime greater than 0.35 g of CaO per liter, this material was absent. The reason for its presence from *E* to *F* and absence from *F* to *G* along the curve *EFG* of figure 5 will become more evident following the discussions of the role of hydrated alumina in the system CaO-Al_2O_3-H_2O.

Thorvaldson, Grace, and Vigfusson [9] found that the compound $3CaO.Al_2O_3.6H_2O$ dissolved to the extent of 0.246 and 0.268 g of anhydrous tricalcium aluminate per liter of water at temperatures of

21° and 40° C, respectively. The solubility at 21° C is equivalent to 0.153 g of CaO and 0.093 g of Al_2O_3 per liter, and this value is plotted herein as a closed triangle symbolized by the letter *T* in figure 5. This point falls on the $3CaO.Al_2O_3$-composition line.

Nacksen and Mosebach [31] have reported the solubility of the isometric hexahydrate as being 0.6774 g of $CaO.Al_2O_3$ per liter at a temperature of 23° C; a value over twice that of any of those mentioned. Their value, which is the average of several separate determinations, is plotted in figure 5 and is represented by the symbol *N–1*. Note that it falls on the curve showing the solubility of the hexagonal hydrated calcium aluminates.

In their determinations, Nacken and Mosebach shook anhydrous tricalcium aluminate (actually 2.93 $CaO.Al_2O_3$) with water for periods as long as 2 months. It is well known that when tricalcium aluminate is hydrated with water hexagonal crystals are formed which, more or less rapidly, depending on the temperature, change to the isometric form. Nacken and Mosebach commented on the silky appearance (usually characteristic of the platy hexagonal crystals) of their mixtures during the first few days of shaking and showed that the dissolved CaO plus Al_2O_3 was greater than 0.6774 g per liter, the average value obtained by shaking for about 2 months. In one instance it reached a value of 0.7792 g per liter. These higher solubility values lie in the region above that of the hexagonal solubility curve. Hence, it would appear that, when the anhydrous tricalcium aluminate first reacted with water, solutions were formed which were unstable with respect to the hexagonal phases. This was followed by a further precipitation of a portion of the CaO and Al_2O_3 as hexagonal material.

Despite the fact that further shaking resulted in a transformation of the bulk of the hydrated material to the isometric hexahydrate, Nacken and Mosebach found that the composition of the solutions remained at the point *N–1* (fig. 5). It should be recalled that the investigations carried out in this laboratory have demonstrated that the approach to equilibrium from supersaturation in regard to the phase $3CaO.Al_2O_3.6H_2O$ is a very slow process.

In a later publication, Nacken and Mosebach [32] carried out two solubility determinations of $3CaO.Al_2O_3.6H_2O$, starting, in these cases, with the hexahydrate itself rather than with the anhydrous tricalcium aluminate. The values they obtained are indicated by the symbols *N–2* and *N–3* in figure 5 and pertain to their experiments 8 and 9, respectively. These solubility values are of the order of magnitude of those obtained by others, in marked contrast to the higher solubility (*N–1*) when the hexagonal crystals are formed as an intermediate phase. Notwithstanding, Nacken and Moseback considered that their higher solubility value (*N–1*) was correct.

They also carried out some experiments pertaining to the composition of solutions resulting from the reaction between CaO plus $3CaO.Al_2O_3$ plus water. Points *N–4* and *N–5* of figure 5 represent the compositions of the solutions they obtained by shaking duplicate mixtures containing 0.31 g of CaO plus 2.705 g of $3CaO.Al_2O_3$ in 1 liter of H_2O; and *N–6* and *N–7* are check solubilities obtained with the additions of 0.81 g of CaO to the same quantities of tricalcium aluminate and water. They noted in their experiments the initial formation of the hexagonal phase and its tendency to revert to the isometric phase.

Again, as with *N–1*, the points *N–4* and *N–5* lie close to the metastable solubility curve of the hexagonal hydrates. Points *N–6* and *N–7* are between the solubility curves of the hexagonal and isometric phases. When Nacken and Mosebach added larger quantities of CaO to their mixtures, they observed that the solubility further decreased (*N–8*). When sufficient CaO had been added to give appreciable quantities of $Ca(OH)_2$ as a solid phase (slightly above C), they found but traces of alumina in solution; in agreement with the findings of Bessey [13] and those of the present investigation.

Although Lerch and Bogue [52] did not give the actual solubility of hydrated tricalcium aluminate in a solution saturated with respect to $Ca(OH)_2$, they, nevertheless, showed that there was no indication of the hydrated tricalcium aluminate forming the hydrated tetracalcium aluminate. This again demonstrates that hydrated tricalcium aluminate, and not hydrated tetracalcium aluminate, is the stable phase in a solution saturated with respect to $Ca(OH)_2$.

Since the solubility of $3CaO.Al_2O_3.6H_2O$ is very low in calcium hydroxide solutions approaching saturation with respect to $Ca(OH)_2$, there is no reason to believe that the solubility of coarsely crystalline $Ca(OH)_2$ in such solutions would be detectably different from that in water. No actual determination was made of the solubility of $3CaO.Al_2O_3.6H_2O$ at a concentration of 1.15 g of CaO per liter (*C*, the solubility of coarsely crystalline $Ca(OH)_2$ in water at 21° C), but it appears from experiments 13 and 14 of table 7 that with such a solution the quantity of alumina in solution should be close to 0.0005 g per liter. Accordingly, *Y* of figure 5 is ascribed as the invariant point at 21° C for $3CaO.Al_2O_3.6H_2O$, coarsely crystalline $Ca(OH)_2$, and a solution containing 0.0005 g of Al_2O_3 and 1.15 g of CaO per liter, and finally the very short line *YC* represents the stable solubility curve of $Ca(OH)_2$ in the system.

4. HYDRATED ALUMINA AS A SOLID PHASE IN THE SYSTEM AT 21° C

Thought will now be given to those regions, in the system $CaO\text{-}Al_2O_3\text{-}H_2O$ at 21° C, where hydrated alumina exists as one of the principal phases. This in turn will be followed by a consideration of the changes that occur as the amorphous hydrated alumina initially produced gradually ages and is converted into crystalline gibbsite, $Al_2O_3.3H_2O$.

Mixtures of calcium aluminate-calcium hydroxide solutions were prepared in a manner similar to that already described in the investigation of the system where the hexagonal hydrated calcium aluminates separated as primary phases. Microscopical examinations of the solid phases were made at intervals to follow any changes which might be taking place.

Some of the regions in which hydrated alumina was formed as a solid phase are shown in figure 6. The compositions of the original mixtures are indicated by closed circles, and crosses show the compositions of the solutions after precipitation of a portion of the alumina as a solid phase. Open circles enclosing crosses signify that crystalline hexagonal hydrated aluminates also are present. The figures accompanying the lines connecting the compositions of the original mixtures and those of the solutions subsequently produced give the molar ratios, CaO/Al_2O_3, in the materials precipitated. The

connecting lines do not necessarily reveal the actual course of precipitation. In fact, it is known in many cases that the paths of precipitation are far different from those indicated by these lines. This applies particularly to the metastable solutions that yielded hexagonal aluminates associated with hydrated alumina. For example, it was observed that from those original mixtures in which the molar ratio, CaO/Al_2O_3, was approximately 2, hexagonal hydrates usually crystallized prior to the appearance of hydrated alumina as a solid phase. Therefore, it seems possible, from figure 1, that the course of precipitation from such solutions must at first have been along a path more

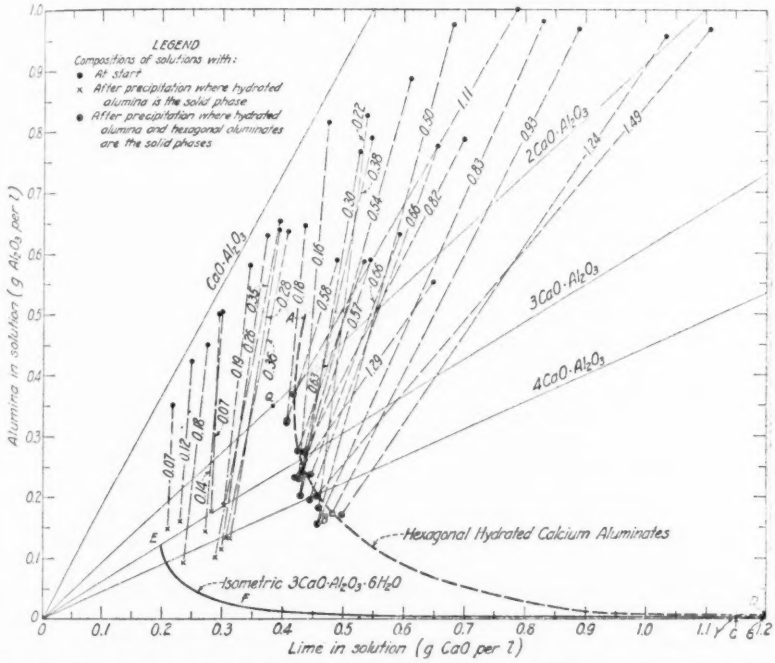
LEGEND
Compositions of solutions with:
At start
After precipitation where hydrated alumina is the solid phase
After precipitation where hydrated alumina and hexagonal aluminates are the solid phases
CaO·Al2O3
2CaO·Al2O3
3CaO·Al2O3
4CaO·Al2O3
Hexagonal Hydrated Calcium Aluminates
Isometric 3CaO·Al2O3·6H2O
Alumina in solution (g Al2O3 per l)
Lime in solution (g CaO per l)

FIGURE 6.—*Some of the regions in the system CaO-Al_2O_3-H_2O at 21° C. in which hydrated alumina is formed as a solid phase.*

or less parallel to the $2CaO.Al_2O_3$-composition line down to some point on the solubility curve of the hexagonal hydrated calcium aluminates, as the hexagonal hydrates crystallized from solution. From this point the path shifted when hydrated alumina separated from solution as a solid phase. But, inasmuch as the hexagonal hydrates were present as solid phases, the path of precipitation proceeded downward along the solubility curve of the hexagonal hydrated calcium aluminates.

However, in most instances in which the molar ratio of CaO/Al_2O_3 was less than 2, it was not possible to follow the actual paths of precipitation, because the hydrated alumina made its appearance either simultaneously with that of the hexagonal hydrates, or so soon thereafter that it was not feasible to filter the mixtures rapidly enough

to ascertain the separate paths of precipitation. It is significant, nevertheless, that the compositions of most of the solutions resulting from the precipitation of both hydrated alumina and the hexagonal hydrates lie fairly well along the solubility curve of the hexagonal hydrated calcium aluminates.

Figure 6 shows that the metastable solutions that decomposed with separation of both hydrated alumina and hexagonal hydrated aluminates contained more than 0.4 g of CaO per liter; i. e., they are located to the right of the solubility curve *ABD* of the hexagonal hydrated calcium aluminates. Furthermore, with two exceptions the compositions of these highly metastable solutions lie between the $CaO.Al_2O_3$- and $2CaO.Al_2O_3$-composition lines. In contrast, the metastable solutions that yielded hexagonal hydrates with no hydrated alumina (see fig. 1) were, with three exceptions, more basic than $2CaO.Al_2O_3$.

Attention will now be directed to the behavior of these calcium aluminate solutions that contained less than 0.4 g of CaO per liter and whose compositions lie to the left of the solubility curve, *ABD* of the hexagonal hydrated calcium aluminates. This set of solutions was prepared by diluting the filtered metastable solutions obtained by shaking anhydrous calcium aluminates or calcium aluminate cements with water, as previously described. Precipitation from those solutions proceeded very slowly, and over 300 days lapsed before the resulting solutions reached the values designated by crosses in figure 6.

The region of precipitation is located between the *AB* section of the curve *ABD* and that section of the solubility curve of the isometric $3CaO.Al_2O_3.6H_2O$ along which the quantity of lime in solution ranges from 0.2 to 0.4 g of CaO per liter. Accordingly, some isometric $3CaO.Al_2O_3.6H_2O$ could be formed as the hydrated alumina precipitated from solution.

If the solubility curves are correctly drawn, no hexagonal hydrates should appear as solid phases when the original mixtures decompose and the system more nearly approaches equilibrium. However, it was observed in several instances that the hexagonal phases actually appeared at first, but later disappeared as the separation of hydrated alumina from solution progressed. This appearance and subsequent disappearance of the hexagonal phase occurred during the early decomposition of those original mixtures which contained approximately 0.4 g of CaO and 0.65 g of Al_2O_3 per liter. Hence, it is thought that the solubility curve of the hexagonal hydrated calcium aluminates should be shifted slightly to the left, and that the curve probably does not bend around so much as indicated. This shifting of the curve is likewise suggested not only by the somewhat lower solubility value of hydrated dicalcium aluminate when equilibrium was approached from undersaturation (see experiment 1 of fig. 2), but also by the still lower solubility value of $2CaO.Al_2O_3.8H_2O$ given by Bessey [13] and indicated by the letter *Q* on the $2CaO.Al_2O_3$-composition line of figure 6.

It should be emphasized again that the hexagonal phases are formed only as intermediate phases in the more gradual approach to real equilibrium. The difficulty of locating accurately the metastable solubility curves of the hexagonal hydrated calcium aluminates should be evident by now, not only because of the separation of hydrated alumina as a solid phase, but also on account of the previously

mentioned transformation of the hexagonal phases into the more stable isometric hydrate $3CaO.Al_2O_3.6H_2O$.

After the hexagonal phases disappeared the course of precipitation apparently moved away from the curve of the hexagonal hydrated calcium aluminates and approached that of the isometric $3CaO.Al_2O_3.6H_2O$. This was accompanied by a slight decrease of lime in solution.

The indices of refraction of the hydrated alumina when first formed although variable, averaged about 1.50, and later increased as the hydrated alumina aged. The hydrated alumina separated from solution as both flakes and pellets, and upon aging the refractive indices of the outside surfaces of both the flakes and pellets increased more rapidly than the interior. Consequently, it was rather difficult to determine the exact indices of refraction. All that can be said is that the refractive indices of the outside shells increased to as much as from 1.56 to 1.58, and that the refractive indices of the interiors of flakes and pellets were definitely less than these values.

It was observed also that the more pronounced increases in indices of refraction in the shells were associated with higher contents of lime in the precipitated materials. This suggested the idea that possibly some of the lime in solution had reacted with the hydrated alumnia which had separated from solution and had formed small amounts of the isometric $3CaO.Al_2O_3.6H_2O$ within the shell of the flakes and pellets. The reaction, however, appeared not to have proceeded far enough to have raised the indices to 1,605, the value for $3CaO.Al_2O_3.6H_2O$. The indicated limited formation of $3CaO.Al_2O_3.6H_2O$ can account only in part for the increase in refractive index of the hydrated alumina upon aging. It does not explain the increases where very small quantities of lime were present in the precipitated products. This must be attributed to a change taking place in the hydrated alumina itself.

In a previous study of the products formed in the reaction of water with calcium aluminates and calcium aluminate cements [1], it was pointed out that the refractive indices of the hydrated alumina obtained ranged from about 1.48 to 1.57. Attention was called to the fact that the index 1.57 agreed fairly well with the mean refractive index of gibbsite, $\alpha=1.566$, $\gamma=1.587$, $\beta=1.556$ [33]. It was also mentioned that Fricke and Wever [34] and Böhm and Niclassen [35], by means of X-ray diffraction patterns, had shown that aged hydrated alumina was crystalline.

Assarsson [36] later found that the hydrated alumina which separated from the calcium aluminate solutions likewise had similar variable indices of refraction and that the index of refraction of the outer layers of the concentric shells of the spherulites was higher than that of the inner. He demonstrated by means of X-ray analysis that the hydrated alumina upon aging exhibited the detectable crystal structure of gibbsite, the complete structure of which was worked out by Megaw [37]. Assarsson came to the conclusion that gibbsite was the final product of the aging, even though some of his samples of hydrated alumina contained between 3 and 4 moles of H_2O rather than the prescribed 3 moles for gibbsite, $Al_2O_3.3H_2O$. The extra water he ascribed to absorbed water rather than to constitutional water of crystallization.

Likewise, X-ray diffraction patterns of samples of aged hydrated alumina were found in the present investigation to contain the lines

characteristic of gibbsite. The intensity of the lines increased as the hydrated alumina aged. It was noted also that the moles of water were in many instances somewhat greater than 3. In addition, the molar ratio, H_2O/Al_2O_3, increased with that of the CaO/Al_2O_3 in the products. Whether the simultaneous increase in molar ratio, H_2O/Al_2O_3, is in part caused by the formation of small quantities of $3CaO.Al_2O_3.6H_2O$ in the shell of the pellets and flakes of hydrated alumina is not known. If $3CaO.Al_2O_3.6H_2O$ was thus formed, it was not present in sufficient quantities to give rise to lines characteristic of this compound in the X-ray diffraction patterns studied.

X-ray diffraction patterns were also obtained of precipitates that had aged a long time before filtering and which contained both hydrated alumina and the hexagonal aluminate. Again, the presence of gibbsite was indicated.

Dilute monocalcium aluminate solutions having less than 0.15 g of CaO per liter remained clear for months and showed but little tendency to liberate hydrated alumina as a solid phase. No attempt was made to see to what extent they might have decomposed had they been "seeded" with gibbsite.

From these studies it can be concluded that hydrated alumina is one of the solid phases formed, and that on aging it is converted to crystalline gibbsite. Furthermore, the aging at 21° C is a very slow process, and, accordingly, a very long time must elapse before true equilibrium is attained. It is evident from the scattered points of figure 6 that equilibrium had not been reached even though the mixtures has stood for over 300 days. Therefore, it was decided to investigate the solubility of gibbsite at increasing concentrations of lime by starting with well-crystallized gibbsite, rather than by continuing the very slow approach to equilibrium from supersaturation.

5. GIBBSITE, $Al_2O_3.3H_2O$, IN THE SYSTEM AT 21° C

The synthetically prepared $Al_2O_3.H_2O$ used in this study was thoroughly washed with water to remove small quantities of alkali salts. The loss on ignition after drying at a temperature of 110° C was 34.50 percent (theoretical H_2O, 34.65 percent). The indices of refraction of the dried material were: $\alpha=1.573\pm0.003$; β, not determined; $\gamma=1.592$ 0.003; and are slightly higher than the values $\alpha=1.566$, $\beta=1.566$, $\gamma=1.587$, as listed by Larsen and Berman [33] for gibbsite. There was a trace of undetermined material with a mean index of refraction somewhat greater than 1.62, but less than 1.63. An X-ray diffraction pattern gave the lines characteristic of gibbsite.

A series of reaction mixtures, containing in each case 2.000 g of gibbsite per liter of solution of calcium hydroxide, was prepared and placed in tightly stoppered flasks. The concentration of the calcium hydroxide solutions ranged from the equivalent of 0.050 g to that of 1.300 g of CaO per liter. The mixtures were maintained at a temperature of 21° C and were shaken from time to time to facilitate an approach to equilibrium. At various intervals of time, aliquots of the solutions were taken for analysis. The compositions of the solutions are given in table 8.

The solubility determinations up to and including those where the initial concentration of lime was 0.300 g of CaO per liter (experiments 1 to 17, inclusive) indicate that no solid phase other than

gibbsite is present. In no instance was more than 0.01 g of CaO removed from solution. At a concentration of 0.350 g of CaO per liter, slightly more lime was removed from solution at the later periods. In experiment 20 this amounted to 0.019 g of CaO. When the gibbsite was placed in the more concentrated calcium hydroxide solutions (experiments 21 to 46, inclusive), greater quantities of lime were removed from solution. In experiment 46, at the end of 810 days, the concentration of lime had been reduced from 1.300 to 0.320 g of CaO per liter.

TABLE 8.—*Solubility of gibbsite,* $Al_2O_3.3H_2O$, *at 21° C*

[Obtained from mixtures containing 2 g of gibbsite per liter of aqueous solution of calcium hydroxide.]

Experiment	Composition of calcium hydroxide solution	Time to approach equilibrium	Composition of resulting solution		Molar ratio, CaO/Al_2O_3, in solid phase
	g of CaO/*liter*	*Days*	*g of* Al_2O_3/*liter*	*g of* CaO/*liter*	
1	0.050	86	0.005	0.047	0.004
2	.050	249	.004	.047	.004
3	.050	810	.005	.046	.006
4	.100	14	.002	.092	.010
5	.100	249	.008	.094	.009
6	.100	439	.007	.100	.0
7	.150	60	.007	.144	.008
8	.150	249	.005	.143	.010
9	.200	14	.005	.192	.010
10	.200	249	.010	.193	.010
11	.200	439	.011	.195	.010
12	.250	87	.008	.243	.010
13	.250	219	.017	.243	.010
14	.250	439	.015	.240	.030
15	.300	60	.009	.290	.010
16	.300	93	.016	.291	.010
17	.300	249	.014	.291	.010
18	.350	87	.017	.344	.008
19	.350	219	.018	.336	.02
20	.350	439	.019	.331	.03
21	.450	87	.016	.435	.02
22	.450	189	.025	.413	.05
23	.450	249	.027	.395	.08
24	.450	439	.017	.326	.17
25	.500	60	.014	.484	.008
26	.500	93	.022	.455	.06
27	.500	189	.032	.436	.09
28	.500	441	.023	.377	.17
29	.605	133	.034	.552	.08
30	.605	244	.040	.536	.10
31	.605	353	.040	.500	.15
32	.706	133	.041	.645	.12
33	.706	244	.054	.616	.13
34	.706	353	.047	.603	.15
35	.900	14	.008	.842	.08
36	.900	60	.031	.804	.14
37	.900	93	.037	.739	.23
38	.900	189	.057	.649	.36
39	.900	334	.047	.594	.44
40	.900	441	.040	.542	.51
41	1.300	14	.008	1.219	.11
42	1.300	60	.019	0.998	.43
43	1.300	189	.031	.654	.92
44	1.300	334	.042	.544	1.09
45	1.300	441	.037	.477	1.18
46	1.300	810	.018	.320	1.48

Equilibrium appears to have been attained in the mixtures that initially contained 0.350 g or less of CaO per liter (experiments 1 to 20, inclusive). Where the concentrations were greater than 0.350 g of CaO per liter, the dissolved alumina at first increased as the lime was removed from solution, reached a maximum, and then decreased.

The course of these changes is shown in figure 7, where the alumina in solution is plotted against the lime in solution. The numbers accompanying the indicated compositions refer to the time, in days, that had lapsed since the mixtures were prepared. A smooth curve (*HFJ*) has been drawn through the points pertaining to the maximum solubility values of alumina.

The solubility curve *EFG* of the isometric $3CaO.Al_2O_3.6H_2O$ and a portion of that of the hexagonal hydrated calcium aluminates have been replotted to fit the enlarged scale used in figure 7 for grams of Al_2O_3 per liter.

The curve HFJ intersects *EFG* where the alumina in solution is 0.02 g of Al_2O_3 per liter and the lime in solution approximately 0.33 g

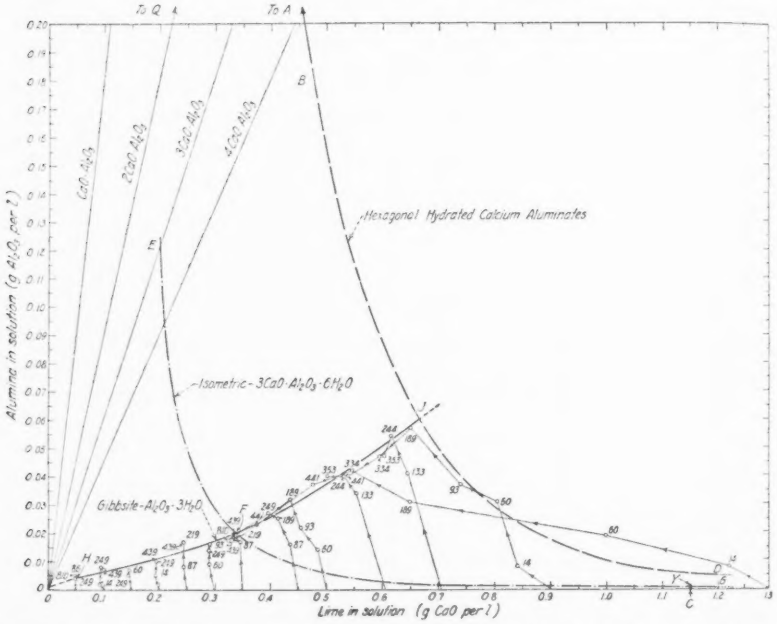

FIGURE 7.—*Composition of solutions formed when gibbsite,* $Al_2O_3.3H_2O$, *was placed in calcium hydroxide solutions of increasing concentrations; maintained at a temperature of 21° C for the time periods, in days, indicated by the numbers.*

of CaO per liter. This point of intersection, *F*, should represent, therefore, the invariant point $3CaO.Al_2O_3.6H_2O$-$Al_2O_3.3H_2O$ (gibbsite). Consequently, gibbsite is the stable phase in the system CaO-Al_2O_3-H_2O at 21° C up to a concentration of lime of 0.33 g of CaO per liter (*HF*), and the isometric $3CaO.Al_2O_3.6H_2O$ is the stable phase beyond 0.33 g of CaO per liter (*FG*). Thus, it becomes apparent why gibbsite dissolves in calcium hydroxide solutions up to concentrations of 0.33 g of CaO per liter without removing lime from solution, and also why hydrated alumina was observed as a solid phase in the solubility determinations of $3CaO.Al_2O_3.6H_2O$ along the metastable segment *EF* of the curve *EFG*.

Since *F* is the invariant point $3CaO.Al_2O_3.6H_2O$-$Al_2O_3.3H_2O$, then in mixtures of gibbsite and calcium hydroxide solutions more

concentrated than 0.33 g of CaO per liter, the CaO would eventually be reduced to this value, and the alumina in solution would reach a value of 0.02 g of Al_2O_3 per liter. Three of the mixtures appear to have arrived very closely to *F*. They are indicated by experiments 20, 24, and 46 of table 8, where the initial concentrations of calcium hydroxide solutions were 0.350, 0.450, and 1.300 g of CaO per liter, respectively. Although the other mixtures had not attained final equilibrium, they appear from figure 7 to be approaching *F*. The mechanism of this approach to the invariant point *F* from mixtures containing more than 0.33 g of CaO per liter seems to be as follows: First, the gibbsite rather slowly dissolves in the solutions of calcium hydroxide, but, inasmuch as $3CaO.Al_2O_3.6H_2O$ is the stable phase rather than gibbsite, some of the lime in solution reacts with either the dissolved alumina or solid gibbsite with the ultimate production of some $3CaO.Al_2O_3.6H_2O$. Consequently, the reactions are taking place at an ever-decreasing concentration of lime. Eventually, however, the composition of the solution reaches some point along the metastable segment *FJ* of the curve *HFJ*, since the rate of solution of gibbsite exceeds the rate of formation of $3CaO.Al_2O_3.6H_2O$. Having reached *FJ*, the path proceeds downward along *FJ* to *F* as this process of formation of $3CaO.Al_2O_3.6H_2O$ and dissolving of gibbsite continues.

Attention will now be directed to the paths followed by two of the reaction mixtures. Experiments 35 to 40, inclusive, pertain to the mixtures starting with a concentration of calcium hydroxide of 0.900 g of CaO per liter. Figure 7 shows that at the end of 60 days the composition of the solution was very close to the metastable solubility curve of the hexagonal hydrated aluminates. Small amounts of hexagonal plates were observed microscopically. The maximum solubility of alumina was reached at the end of 189 days (experiment 38), and the composition is near the point *J*. The path then proceeded downward along *FJ* toward *F*, but, even at the end of 441 days, less than half of the distance to *F* had been covered. During these changes the hexagonal phase disappeared, and the refractive index of the outer shells of the gibbsite crystals increased to about 1.60 because of the formation of some $3CaO.Al_2O_3.6H_2O$.

The mixture prepared with a supersaturated calcium hydroxide solution containing 1.300 g of CaO per liter yielded solutions at the end of 14 and 60 days in the field where the hexagonal phase (probably hydrated tetracalcium aluminate) is formed as a mestastable phase, and hexagonal crystals were observed microscopically. At 189 days the reactions had proceeded to where the composition of the solution was no longer in this region, and the hexagonal phase disappeared. The composition of the solution had not yet reached the metastable section *FJ*, as in the case of the mixtures initially containing 0.900 g of CaO per liter. At the end of 334 days the composition of the solution was on the section *FJ* at a point close to that attained at the end of 441 days by the mixture prepared with calcium hydroxide having 0.900 g of CaO per liter. The path then proceeded along *FJ*, but, in this case, reached the invariant point *F*, but only after a lapse of 810 days. These experiments show the long time required to reach equilibrium, even under rather favorable conditions.

This study of the system CaO-Al_2O_3-H_2O at 21°C may be considered as not entirely complete in that it does not deal with the solubility curves of the hydrates of alumina other than gibbsite, $Al_2O_3.3H_2O$. For example, there are the mineral diaspore ($Al_2O_3.H_2O$); its reported isomer [34, 35, 38, 39, 40, 41, 42, 43, 48], often called "böhmite"; and possibly an isomer of gibbsite $Al_2O_3.3H_2O$ [38, 44, 45, 46, 47, 48, 49], sometimes referred to as bayerite. There seems to be some doubt, however, as to the existence of this last trihydrate. Notwithstanding that there is some difference of opinion among various investigators as to the order of stability of these hydrates of alumina in alkaline solutions, there are considerable data showing that gibbsite is one of the more stable hydrates, if not the most stable, at room temperature. Therefore, gibbsite is perhaps the most important hydrate of alumina in relation to the behavior of cements.

Lea and Bessey [13, 30] are of the opinion that a stable solubility curve for $Al_2O_3.aq$ at 25°C coincides with the $3CaO.Al_2O_3$-composition line from *O* to *E* (fig. 6). The point *E*, or a point very close to *E*, is, according to Lea and Bessey, the invariant point $3CaO.Al_2O_3.6H_2O$-$Al_2O_3.aq$. They also suggest that the solubility curve for $Al_2O_3.aq$ then proceeds from *E* to *Q* (see figure 6 for location of *Q*), and that *Q* is the metastable invariant point $2CaO.Al_2O_3.8H_2O$-$Al_2O_3.aq$. Jones [51] points out, however, that the stable section for the solubility of $Al_2O_3.aq$, as given by Lea and Bessey, pertains to the gel form, and the solubility curve with respect to crystalline $Al_2O_3.3H_2O$ must fall below this. Our studies have demonstrated that Jones is correct, and it has been shown that *HF* (fig. 7) is the stable solubility curve for $Al_2O_3.3H_2O$ (gibbsite) and that the stable invariant point between $3CaO.Al_2O_3.6H_2O$ and gibbsite is at *F*.

IV. STUDIES OF THE SYSTEM CaO-Al_2O_3-H_2O AT 90° C

1. HEXAGONAL HYDRATED CALCIUM ALUMINATES IN THE SYSTEM AT 90° C

In the investigation of the system CaO-Al_2O_3-H_2O at 21°C, it was shown that the hexagonal phases were metastable. The hexagonal phases become less stable with rising temperature, and are so unstable at 90°C that no attempt was made to study their solubility relationships.

2. ISOMETRIC TRICALCIUM ALUMINATE HEXAHYDRATE, $3CaO.Al_2O_3.6H_2O$, IN THE SYSTEM AT 90° C

Despite the fact that the hexagonal phases are so unstable at 90°C that it was not feasible to determine their solubilities, nevertheless, once they are formed, they persist in small amounts for some time, even in the presence of the $3CaO.Al_2O_3.6H_2O$, into which they are eventually converted. For this reason, it seemed preferable to investigate the solubility of the isometric aluminate by placing this solid phase in solutions of calcium hydroxide and heating the mixtures to 90°C rather than to attempt to approach equilibrium from supersaturation by mixing together metastable calcium aluminate solutions and calcium hydroxide solutions heated to 90°C.

The mixtures, which contained 2 g of $3CaO.Al_2O_3.6H_2O$ per liter of calcium hydroxide solutions of varied concentrations, were placed on a steam bath in well-stoppered flasks provided with soda-lime adsorption tubes. Aliquots of the aqueous phase were taken at intervals for analysis. Equilibrium appeared to be attained much sooner at a temperature of 90° C than at 21° C, and table 9 gives the quantities of alumina and lime in the aqueous phase at the end of 4 to 5 days. Because the calcium hydroxide solutions attacked the glass of the containers somewhat at 90° C, the small quantities of silica were removed prior to the determination of alumina.

In experiments 5 and 6 the concentrations of the calcium hydroxide solutions were decreased from the equivalent of 0.856 g and 1.112 g of CaO per liter to 0.628 g and 0.638 g of CaO per liter, respectively, and finely divided crystalline $Ca(OH)_2$ was found mixed with $3CaO.Al_2O_3.6H_2O$.

TABLE 9.—*Solubility of isometric tricalcium hexahydrate,* $3CaO.Al_2O_3.6H_2O$, *at 90° C.*

[Initial mixtures: 2 g of $3CaO.Al_2O_3.6H_2O$ per liter of calcium hydroxide solution]

Experiment	Composition of calcium hydroxide solutions	Composition of final solutions		Remarks
		Al_2O_3	CaO	
	g of CaO /liter	*g/liter*	*g/liter*	
1	0	0.190	0.306	
2	.250	.089	.335	
3	.390	.073	.381	
4	.500	.029	.509	
5	.856	.013	.628	Finely crystalline $Ca(OH)_2$ present.
6	1.112	.017	.638	Finely crystalline $Ca(OH)_2$ present.

In figure 8 the solubility values of $3CaO.Al_2O_3.6H_2O$ are plotted as grams of Al_2O_3 per liter versus grams of CaO per liter, and a curve, *KLM*, has been drawn to approximate the points representing these compositions. A comparison of figure 8 with figure 5 shows that $3CaO.Al_2O_3.6H_2O$ is more soluble at 90° than at 21° C. At 21° C, however, the curve extends to higher lime concentrations than at 90° C because the solubility of $Ca(OH)_2$ decreases with an increase in temperature.

M represents the invariant point for $3CaO.Al_2O_3.6H_2O$, $Ca(OH)_2$, and a solution containing 0.015 g of Al_2O_3 and 0.63 g of CaO per liter (the average of the compositions of the final solutions of experiments 5 and 6 of table 9). This concentration of CaO is about 0.04 g per liter greater than that indicated by *P*, which pertains to the solubility of coarsely crystalline $Ca(OH)_2$ in water at 90° C, as given by Bassett [50]. Connecting *P* with *M* gives the line *PM*, which represents the solubility of $Ca(OH)_2$ in the system at 90° C.

3. GIBBSITE, $Al_2O_3.3H_2O$, IN THE SYSTEM AT 90° C

The role of gibbsite in the system CaO-Al_2O_3-H_2O at 90° C was investigated in a manner similar to that employed in the study of the solubility relationships of $3CaO.Al_2O_3.6H_2O$ at this temperature. The mixtures in these experiments contained 2 g of gibbsite per liter of calcium hydroxide solutions of known but varied concentrations.

The data of experiments 1, 2, and 3 of table 10 show that the solubility of the gibbsite increases as the concentration of the calcium hydroxide increases. In experiments 4 to 8, inclusive, in which the initial concentration of lime in solution was more than 0.3 g of CaO per liter, there was a definite removal of lime from solution. This was manifested also by a change in the solid phases: First, by an increase in the refractive index of the outside layer of the gibbsite particles (experiment 4); followed by the appearance of increasing quantities of $3CaO.Al_2O_3.6H_2O$, which became better crystallized as the concentra-

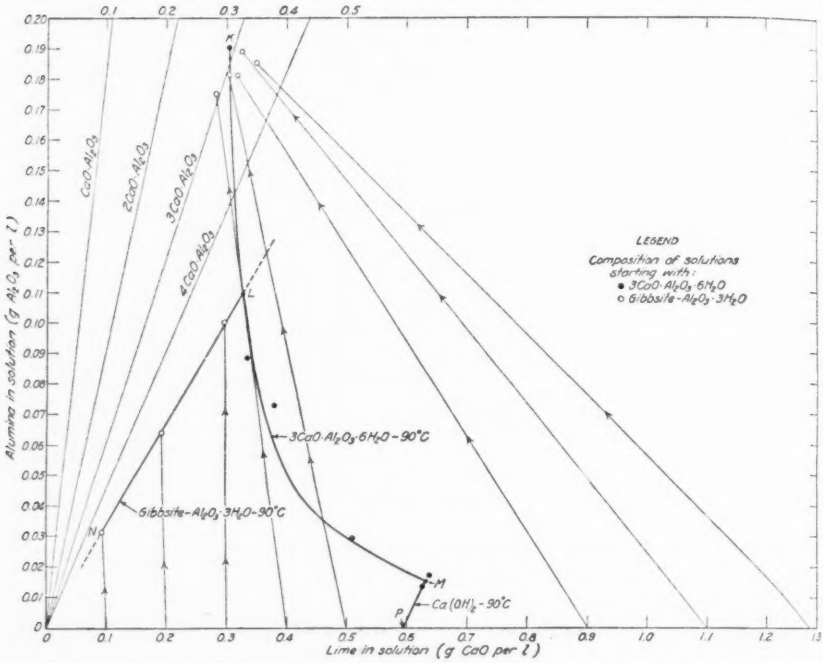

FIGURE 8.—*Composition of solutions formed when isometric* $3CaO.Al_2O_3.6H_2O$ *and gibbsite,* $Al_2O_3.3H_2O$, *were placed, separately, in calcium hydroxide solutions of increasing concentrations; maintained at a temperature of 90° C.*

tion of the calcium hydroxide of the original mixtures increased (experiments 5 to 8, inclusive).

These reactions were attended by a marked increase in the quantity of alumina in solution, from experiment 3, where the initial concentration of the calcium hydroxide was equivalent to 0.300 g of CaO per liter, to experiments 4 to 8, inclusive, where the concentrations of the calcium hydroxide were higher than this. Furthermore, the quantities of alumina in solution in experiments 4 to 8, inclusive, were almost identical, and the lime in solution had been reduced to concentrations of about 0.3 g of CaO per liter in these same mixtures. The compositions of these resulting solutions were approximately the same as that attained when $3CaO.Al_2O_3.6H_2O$ was dissolved in water at 90° C (see table 9, experiment 1).

TABLE 10.—*Solubility of gibbsite,* $Al_2O_3.3H_2O$, *at 90° C*

[Initial mixtures: 2 g of gibbsite per liter of calcium hydroxide solution.]

Experiment	Composition of calcium hydroxide solutions	Composition of final solutions		Remarks
		Al_2O_3	CaO	
	g of CaO*/liter*	*g/liter*	*g/liter*	
1	0.100	0.031	0.092	Indices of refraction unchanged.
2	.200	.063	.189	Do.
3	.300	.099	.294	Do.
4	.400	.175	.283	Indices of refraction raised
5	.500	.178	.298	Small amount of $3CaO.Al_2O_3.6H_2O$.
6	.900	.178	.319	Considerable $3CaO.Al_2O_3.6H_2O$.
7	1.101	.189	.327	Do.
8	1.284	.178	.353	Do.

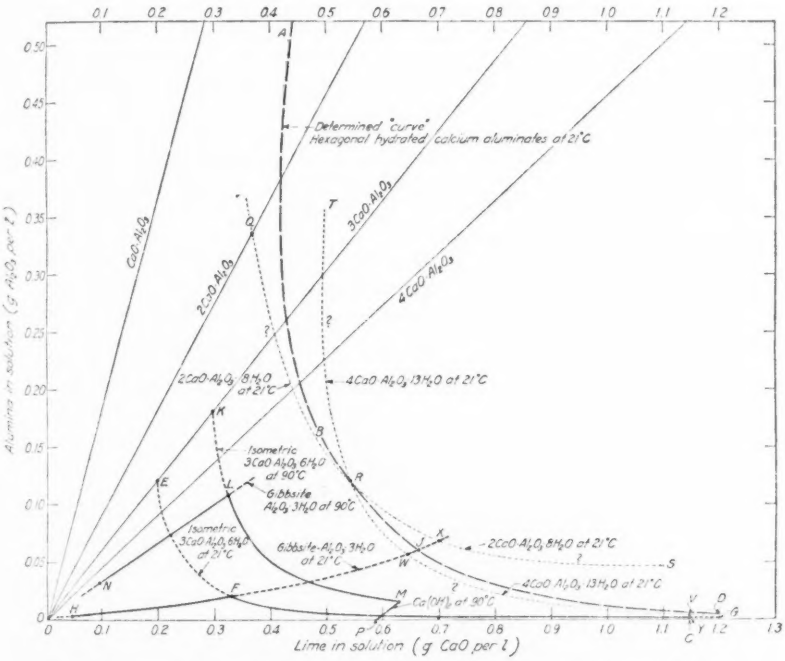

FIGURE 9.—*System* CaO-Al_2O_3-H_2O *at temperatures of 21° and 90° C.*

The curves and points are as follows:

ABD, Metastable solubility "curve" for mixtures of the hexagonal hydrates $2CaO.Al_2O_3.8H_2O$ and $4CaO.Al_2O_3.13H_2O$ at 21° C; *QRS*, suggested metastable solubility curve for hexagonal hydrate $2CaO.Al_2O_3.8H_2O$ at 21° C; *Q*, approximate solubility of hexagonal hydrate $2CaO.Al_2O_3.8H_2O$, apparently congruent, in water at 21° C, (Bessey [13]); *TRV*, suggested metastable solubility curve for hexagonal hydrate $4CaO.Al_2O_3.13H_2O$ at 21° C; *R*, suggested metastable invariant point $2CaO.Al_2O_3.8H_2O$-$4CaO.Al_2O_3.13H_2O$ at 21° C; *C*, solubility of coarsely crystalline $Ca(OH)_2$ in water at 21° C; *V*, approximate metastable invariant point $4CaO.Al_2O_3.13H_2O$-$Ca(OH)_2$ at 21° C; *EFG*, solubility curve of isometric hydrate $3CaO.Al_2O_3.6H_2O$ at 21° C, with *EF* metastable with respect to gibbsite; and *FG* the stable section. (See also, Bessey [13]); *Y*, stable invariant point $3CaO.Al_2O_3.6H_2O$-$Ca(OH)_2$ at 21° C, *YC*, solubility curve of $Ca(OH)_2$ at 21° C, *HFJ*, solubility curve of gibbsite, $Al_2O_3.3H_2O$ at 21° C, with *HF* the stable section; and *FJ* metastable with respect to $3CaO.Al_2O_3.6H_2O$; *F*, stable invariant point $3CaO.Al_2O_3.6H_2O$-$Al_2O_3.3H_2O$ (gibbsite) at 21° C; *W*, suggested metastable invariant point $4CaO.Al_2O_3.13H_2O$-$Al_2O_3.3H_2O$ (gibbsite) at 21° C; *X*, possible metastable invariant point $2CaO.Al_2O_3.8H_2O$-$Al_2O_3.3H_2O$ (gibbsite) at 21° C; *KLM*, solubility curve of isometric hydrate $3CaO.Al_2O_3.6H_2O$ at 90° C; *M*, stable invariant point $3CaO.Al_2O_3.6H_2O$-$Ca(OH)_2$ at 90° C; *NL*, solubility of $Al_2O_3.3H_2O$ (gibbsite) at 90° C; *L*, stable invariant point $3CaO.Al_2O_3.6H_2O$-$Al_2O_3.3H_2O$ at 90° C; *P*, solubility of coarsely crystalline $Ca(OH)_2$ in water at 90° C, (Basset [50]); *PM*, solubility curve of $Ca(OH)_2$ at 90° C.

This status of gibbsite in the system CaO-Al_2O_3-H_2O at 90° C is illustrated in figure 8, which also shows the solubility relations of the $3CaO.Al_2O_3.6H_2O$ at this temperature. The straight line drawn through the compositions of the solutions resulting from dissolving of gibbsite in calcium hydroxide in concentrations equivalent to 0.100, 0.200, and 0.300 g of CaO per liter (table 10, experiments 1 to 3, inclusive), when extended, cuts the solubility curve *KLM* of $3CaO.Al_2O_3.6H_2O$ at *L*. Consequently, *L* must be the invariant point for $3CaO.Al_2O_3.6H_2O$, gibbsite ($Al_2O_3.3H_2O$), and the solution which has the approximate composition of 0.11 g of Al_2O_3 and 0.33 g of CaO per liter.

V. DISCUSSION OF THE SYSTEM CaO-Al_2O_3-H_2O OVER THE TEMPERATURE RANGE 21° TO 90° C

In describing the investigations on the system CaO-Al_2O_3-H_2O, the outline which has been followed has of necessity entailed discussions of the solubility relations of the various phases, more or less separately. It now seems advisable to deal with the system as a whole over the temperature range of 21° to 90° C. For this purpose the solubility curves that are considered to be established are shown in figure 9. In addition, certain curves have been sketched lightly in the diagram to facilitate a more complete understanding of the probable metastable solubility relationships of the hexagonal dicalcium and tetracalcium hydrated aluminates.

No attempt has been made to conjecture as to where the probable metastable curves of the hexagonal hydrated calcium aluminates at 90° C may be placed in the diagram, owing to the decided instability of these forms at this temperature. It must be admitted that the so-called solubility curve, *ABD*, of the hexagonal forms at 21° C was drawn, in the first place, merely for convenience of discussion. Other than serving to indicate the approximate overlapping solubilities of the mixtures of the hydrated dicalcium and tetracalcium aluminates, it has no significance per se. The X-ray studies revealed that *ABD* must pertain to mixtures of dicalcium and tetracalcium aluminates.

In the discussion of the hexagonal hydrated calcium aluminates, it was pointed out that a metastable invariant point for $2CaO.Al_2O_3.8H_2O$, $4CaO.Al_2O_3.13H_2O$, and solution was believed to lie somewhere between about 0.5 and 0.6 g of CaO and about 0.10 and 0.15 g of Al_2O_3 per liter. For convenience, this point is arbitrarily fixed at *R* in figure 9. At concentrations of lime less than that indicated by *R*, the mixture of solid phases is composed predominantly of the dicalcium compound, whereas at the higher line comcentrations the tetracalcium aluminate constitutes the greater proportion of the solid phases.

If consideration now be given to the relations of the metastable hexagonal hydrated aluminates in regard to the other phases in the system, it is evident that there can be no stable equilibrium curves for these two aluminates, since they exist only as metastable phases. If attempts were to be made to secure sufficient data with the hope of establishing a metastable curve of the hydrated dicalcium aluminate free of the hydrated tetracalcium aluminate, it is clear that hydrated alumina, or the isometric hydrate, or both, very probably would make their appearance and defeat the object in view. Similar difficulties would be encountered with the hydrated tetracalcium aluminate.

Inasmuch as the actual determinations of these separate metastable solubility curves hold but little promise of success, it may not be amiss to sketch diagrammatically (fig. 9) how it is thought these metastable curves may be located with respect to one another, as well as to the experimental curve *ABD*.

The point *Q* in figure 9 indicates the solubility of $2CaO.Al_2O_3.8H_2O$ in water, as reported by Bessey [13]. This is somewhat lower than the point of intersection of the curve *ABD* with the $2CaO.Al_2O_3$.-composition line, as might be expected, since *ABD* was constructed from the data of solutions resulting from an approach from supersaturation.

Connecting *Q* and *R*, as shown in figure 9, gives a curve which will be ascribed as a section of a diagrammatic metastable curve for $2CaO.Al_2O_3.8H_2O$ at 21°C where this aluminate is more stable than the hydrated tetracalcium aluminate. Beyond *R* the curve should proceed along some path (*RS*) where this aluminate is less stable than the tetracalcium aluminate. Accordingly, at each concentration of lime in this region the concentration of alumina in a solution saturated with respect to the dicalcium aluminate will be greater than the quantity of alumina in a solution saturated with respect to the tetracalcium aluminate. By analogy, a suggested metastable solubility curve (TRV) for $4CaO.Al_2O_3.13H_2O$ is diagrammatically represented as shown. The point *V* is a suggested metastable invariant point for $4CaO.Al_2O_3.13H_2O$-$Ca(OH)_2$.

As demonstrated previously, *EFG* represents the solubility of $3CaO.Al_2O_3.6H_2O$ and *HFJ*, that of gibbsite, $Al_2O_3.3H_2O$, at 21°C. The point *F* is the stable invariant point for these two solid phases. Since *FJ* represents the metastable solubility of gibbsite, *W* becomes a metastable invariant point, $4CaO.Al_2O_3.13H_2O$-$Al_2O_3.3H_2O$; and on extending *FJ* to *X*, a second metastable invariant point, $2CaO.Al_2O_3.8H_2O$-$Al_2O_3.3H_2O$, is reached. It should be borne in mind that these two metastable invariant points are not established because the actual locations of the metastable curves, as stated previously, have not been determined.

It can be seen from the diagram that, if the concentration of lime is maintained in excess of 0.33 g of CaO per liter at a temperature of 21°C, gibbsite must eventually disappear as a solid phase and be converted into the isometric $3CaO.Al_2O_3.6H_2O$, which is the only stable phase in the region extending from a concentration of lime beyond 0.33 g of CaO per liter up to 1.15 g of CaO per liter. The solubility curve of $3CaO.Al_2O_3.6H_2O$ has been extended slightly beyond C (for solutions supersaturated with respect to coarsely crystalline $Ca(OH)_2$ can easily be prepared); but, at true equilibrium, crystalline $Ca(OH)_2$ would also appear as a solid phase, and the concentration of lime in solution would be reduced to 1.15 g of CaO per liter. The alumina in solution at this invariant point, Y, is but 0.0005 g per liter. The very short line *YC* represents the solubility of $Ca(OH)_2$ at 21°C.

To represent properly the effect of temperature on the solubility relationships of the various phases in the system CaO-Al_2O_3-H_2O, one perhaps should resort to a space model. However, as the system is rather simple at 90°C, it was felt that a clear presentation could be made merely by projecting the solubility curves of the isometric tricalcium aluminate hexahydrate, gibbsite, and $Ca(OH)_2$ onto

the diagram at 21°C. Accordingly, in figure 9, *KLM* shows the role of the isometric aluminate, *NL* that of the gibbsite, and *PM* that of $Ca(OH)_2$ at 90°C.

The solubility of both the isometric hydrated aluminate and gibbsite increase with an increase in temperature from 21° to 90° C. The increases in solubility are such that the invariant point at 90° C (*L*), $3CaO.Al_2O_3.6H_2O$, $Al_2O_3.3H_2O$ (gibbsite), and solution occurs at practically the same lime concentration as at 21° C (*F*), namely, 0.33 g of CaO per liter.

It follows that, at temperatures between 21° and 90° C, there is a family of curves for $3CaO.Al_2O_3.6H_2O$ and $Al_2O_3.3H_2O$ (gibbsite), with each pair intersecting at invariant points of constant lime concentration (0.33 g of CaO per liter), but of increasing concentration of alumina (from 0.02 g of Al_2O_3 to 0.11 g of Al_2O_3 per liter) with increase in temperature.

Hence, at temperatures between 21° and 90° C, gibbsite is the stable solid phase up to a concentration of lime in the aqueous phase of 0.33 g of CaO per liter. At concentrations of lime greater than this, $3CaO.Al_2O_3.6H_2O$ becomes the stable phase, but the limit of concentration at any given temperature is ultimately restricted by the solubility of $Ca(OH)_2$ at that temperature. Consequently, there is a series of invariant points between 21° and 90° C for $3CaO.Al_2O_3.6H_2O$, $Ca(OH)_2$, and solutions whose compositions vary continuously from *Y* (1.15 g of CaO and 0.0005 g of Al_2O_3 per liter) to *M* (0.63 g of CaO and 0.015 g of Al_2O_3 per liter). For solubility values of $Ca(OH)_2$ in water between 21° and 90° C, one should consult Bassett [50].

Even though this investigation covers most of the salient factors pertaining to the system $CaO-Al_2O_3-H_2O$ between temperatures of 21° and 90° C, nevertheless, the possible role of certain hydrates other than those encountered in this study of the system should be considered.

Travers and Sehnoutka [17], and later, Mylius [8] have described a tricalcium aluminate 18-hydrate, $3CaO.Al_2O_3.18H_2O$, occurring as fine needles, orthohombic and biaxial negative. This hydrate has been prepared only by precipitation from potassium aluminate solutions and has never been perceived either upon the addition of solutions of calcium hydroxide to calcium aluminate solutions or in the hydration of calcium aluminates. Accordingly, it appears that this compound is formed only in the presence of potassium (or sodium) ions or others than those of the hydrated calcium aluminates, and consequently is unstable in the system $CaO-Al_2O_3-H_2O$.

In addition, there is the so-called pentacalcium hydrate, $5CaO.Al_2O_3.34H_2O$, which has been reported only by Assarsson [6, 7, 36], who acknowledged, however, in his discussion of a paper by Bessey [13], that it seems to be impossible to prepare such an aluminate without any trace of sulfate. For this reason, it may be presumed that this hydrate is unstable in the ternary system $CaO-Al_2O_3-H_2O$, but may exist in the quaternary system $CaO-Al_2O_3-CaSO_4-H_2O$ as a metastable phase. For further information on this latter point one should consult the extensive investigation by Jones [51] on this quaternary system at 25° C.

Although the studies of Assarsson [6, 7, 36] seem to indicate the existence of a monocalcium aluminate hydrate of the formula $CaO.Al_2O_3.10H_2O$, this compound has been prepared by precipitation from

monocalcium aluminate solutions only at relatively low temperatures. It does not seem to be stable at a temperature so high as 21° C and was not observed in the present investigation.

Therefore, the foregoing considerations indicate that the three hydrated aluminates, $3CaO.Al_2O_3.18H_2O$, $5CaO.Al_2O_3.34H_2O$, and $CaO.Al_2O_3.10H_2O$, are no factors of moment in the ternary system CaO-Al_2O_3-H_2O from 21° to 90° C, and, if they exist at all in this system, they must be very unstable.

As mentioned earlier, the relation of the biaxial form of the tetracalcium aluminate hydrate to the hexagonal modification in the system CaO-Al_2O_3-H_2O warrants further study, as do those hydrates of alumina other than gibbsite.

VI. SUMMARY

The foregoing investigation included a study of the system CaO-Al_2O_3-H_2O at 21° and 90° C.

The solid phases were investigated by petrographical and X-ray diffraction methods. By means of X-ray diffraction patterns, it was found that the so-called hexagonal tricalcium aluminate hydrate is in reality a mixture of hexagonal $2CaO.Al_2O_3.8H_2O$ and hexagonal $4CaO.Al_2O_3.13H_2O$ intercrystallized in equimolecular proportions. On standing, the dicalcium aluminate hydrate is slowly converted into the tetracalcium aluminate hydrate and hydrated alumina. Loss of water of hydration in the tetracalcium aluminate hydrate results in a decrease in the unit cell along the *c* axis.

Although the di- and tetracalcium aluminate hydrates exist only as metastable phases in the system CaO-Al_2O_3-H_2O between 21° and 90° C, a study was made of their solubility relationships at 21° C. There appears to be a metastable invariant point for these two phases and a solution containing between 0.5 and 0.6 g of CaO per liter and 0.10 and 0.15 g of Al_2O_3 per liter. As the temperature increases the hexagonal aluminates become less stable.

The only stable solid phases that were found in the system CaO-Al_2O_3-H_2O over the temperature range of 21° to 90° C were: gibbsite, $Al_2O_3.3H_2O$; the isometric tricalcium aluminate hexahydrate, $3CaO.Al_2O_3.6H_2O$; and $Ca(OH)_2$. The solubility curves of these phases in the system CaO-Al_2O_3-H_2O were determined at 21° C and at 90° C. Over this range of temperature, gibbsite is the stable phase up to a concentration of 0.33 g of CaO per liter; at concentrations greater than this, the isometric hexahydrate is the only stable phase, until those points are reached at which $Ca(OH)_2$ also appears as a solid phase. The series of invariant points for gibbsite and the isometric phase occurs at a concentration of CaO of 0.33 g per liter, but with the concentration of Al_2O_3 increasing from 0.02 g per liter at 21° C to 0.11 g per liter at 90° C.

In carrying out the work in connection with this paper the authors had the valuable assistance of H. Insley in the microscopical examinations.

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WASHINGTON, January 26, 1943.

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PERFORATED COVER PLATES FOR STEEL COLUMNS: COMPRESSIVE PROPERTIES OF PLATES HAVING A NET-TO-GROSS CROSS-SECTIONAL-AREA RATIO OF 0.33

By Ambrose H. Stang and Martin Greenspan

ABSTRACT

Tests were made to determine the mechanical properties of perforated cover plates intended to be used as a substitute for lattice bars or batten plates in built-up box-type columns. Each test column was built up from one perforated plate and four angles. Two columns had circular and two ovaloid perforations. For each column the ratio of net-to-gross cross-sectional area in the plate was 0.33. In this paper the methods of test are described, and the results of the tests of the four columns are given.

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I. INTRODUCTION

This paper is the sixth of a series dealing with the mechanical properties of perforated cover plates intended to be used as a substitute for lattice bars or batten plates in built-up box-type columns. An outline of the program and results for plates having a net-to-gross cross-sectional-area ratio of 0.55 and having width-to-thickness ratios of 40, 53, and 68 have been given in previous Research Papers.[1]

[1] Ambrose H. Stang and Martin Greenspan, *Perforated cover plates for steel columns: Program and test methods*, J. Research NBS **28**, 669 (1942) RP1473; *Perforated cover plates for steel columns: Compressive properties of plates having ovaloid perforations and a width-to-thickness ratio of 40*, **28**, 687 (1942) RP1474; *Perforated cover plates for steel columns: Compressive properties of plates having ovaloid perforations and a width-to-thickness ratio of 68*, **29**, 279 (1942) RP1501; *Perforated cover plates for steel columns: Compressive properties of plates having ovaloid perforations and a width-to-thickness ratio of 53*, **30**, 15 (1943) RP1514; *Perforated cover plates for steel columns: Compressive properties of plates having circular perforations and a width-to-thickness ratio of 53*, **30**, 177 (1943) RP1527.

In this paper are presented the test results for the *C6* and *C7* columns. The plates in these columns were 30 inches wide by ⅜ in. thick, thus having a width-to-thickness ratio of 80. The plates of the *C6* columns had circular perforations 10 in. in diameter and those of the *C7* columns ovaloid perforations 10 in. wide. The net-to-gross cross-sectional-area ratio was 0.33.

The columns had been riveted and the column ends planed before delivery to the laboratory.

The dimensions and areas were determined, and the testing procedures and methods of calculation for the coupons and columns were made in the same manner as for the perforated-plate columns previously tested,[2] except for those procedures which differed because the plates and angles of the columns had been riveted together or because columns without perforations had not been prepared.

II. COVER-PLATE COLUMNS

1. GENERAL

The details of the columns are shown in figure 1. There were two *C6* and two *C7* columns. The cutting diagrams for the plate and angle material are also shown in figure 1. The plates for the four columns were all cut from the same length. The four angles for each column were all cut from the same length. The designations for the plates and angles, as indicated by the match marks in the cutting diagrams of figure 1, for the columns are given in table 1.

TABLE 1.—*The plates and angles in the columns*

Column designation	Plate designation	Angle designations
C6A	*F(0-1)*	*A(0-1), A(2-3), A(4-5), A(6-7)*
C6B	*F(2-3)*	*B(0-1), B(2-3), B(4-5), B(6-7)*
C7A	*F(4-5)*	*C(0-1), C(2-3), C(4-5), C(6-7)*
C7B	*F(6-7)*	*D(0-1), D(2-3), D(4-5), D(6-7)*

2. DIMENSIONS

The dimensions given in figure 1 are nominal. Direct measurements of the plates and angles could not be made, since they were riveted together. Measurements[3] of the width and thickness were therefore made on the three separate pieces 2 ft long submitted for coupons for each length. The gross cross-sectional area of each of the four main sections of each length was taken as the average of the cross-sectional areas of the three 2-ft lengths. The net width of the plate was taken as the gross width minus the average of the widths of all the perforations. The net area of the plate was taken as the product of the average thickness and the average net width.

[2] See Research Paper RP1473.
[3] See page 676 of RP1473.

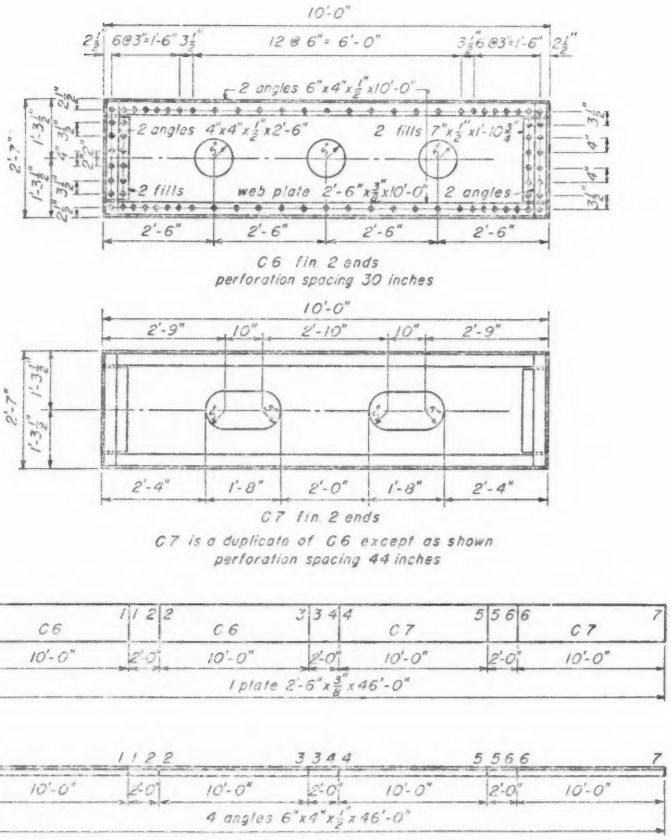

FIGURE 1.—*Details of the C6 and C7 columns and cutting diagrams for the plate and angle material.*

III. PROCEDURE

1. COUPONS

Coupons representing the plate and angle material were cut in the direction of rolling and tested in tension. Young's modulus of elasticity, E; Poisson's ratio, ν; yield point; tensile strength; and elongation were determined.

A composite sample of the material from the *C6* and from the *C7* columns was analyzed for carbon, manganese, phosphorus, and sulfur.

2. COLUMNS

(a) ELASTIC RANGE

The shortening under load in the elastic range was determined for each column, and the modulus E'_p was computed. Since columns similar to the *C6* and *C7* columns, but having an unperforated plate, were not available, the modulus E'_s of hypothetical columns having

the same dimensions as the *C6* and *C7* columns, but having an unperforated plate, was taken as being equal to the weighted average value of Young's modulus of elasticity for the coupons representing the column. The effective area, K, of the perforated plate with respect to shortening under compressive load was computed, using these E_p' and E_s' values.[4]

The strains in the edge of the perforation and in the surfaces of the plate in the bay-length at midheight of the column were determined for columns *C6A* and *C7A*. The distribution of stress in this bay-length for these two columns was calculated from the strain data and the values of the elastic constants obtained from the coupon tests. Figure 2 shows column *C6A* in the testing machine during the test in the elastic range.

(b) MAXIMUM LOAD

Each of the four columns was subjected to a maximum-load test. Data to complete the stress-strain curves and data for stress-deflection curves were taken.

IV. RESULTS

1. COUPONS

The results of the tensile tests of the coupons are given in table 2.

TABLE 2.—*Results of tensile tests of coupons*

Coupon designation	Thickness	Young's modulus of elasticity, E	Poisson's ratio, ν	Yield point	Tensile strength	Elongation in 8 in.
PLATE COUPONS						
	Inch	*Kips/in.²*		*Kips/in.²*	*Kips/in.²*	*Percent*
F(1-2)	0.383	29,500	0.281	37.5	59.3	33.0
F(3-4)	.385	29,600	.281	38.4	59.1	34.8
F(4-5)	.385	29,600	.281	37.9	59.1	33.0
ANGLE COUPONS						
A(1-2)	0.507	29,700	0.290	35.7	61.9	32.0
A(3-4)	.511	29,500	.280	36.9	61.9	33.9
A(5-6)	.503	29,600	.285	35.8	61.2	32.9
B(1-2)	.508	29,600	.291	40.9	68.7	30.9
B(3-4)	.499	29,500	.283	40.6	69.3	26.3
B(5-6)	.513	29,500	.282	41.9	68.7	31.0
C(1-2)	.501	29,800	.290	36.6	64.0	28.7
C(3-4)	.510	29,900	.283	37.8	63.8	31.5
C(5-6)	.505	29,600	.283	37.4	64.0	29.9
D(1-2)	.500	29,700	.282	35.8	59.2	31.8
D(3-4)	.497	29,700	.283	36.6	59.4	32.2
D(5-6)	.501	29,709	.282	35.9	59.3	34.2

The chemical composition of the coupon material is given below.

Composite sample	Carbon	Manganese	Phosphorus	Sulfur
	Percent	*Percent*	*Percent*	*Percent*
Columns *C6*	0.17	0.59	0.007	0.033
Columns *C7*	.22	.71	.017	.033

[4] See page 680 of RP1473.

FIGURE 2.—*Column C6A in the testing machine during the test in elastic range.*

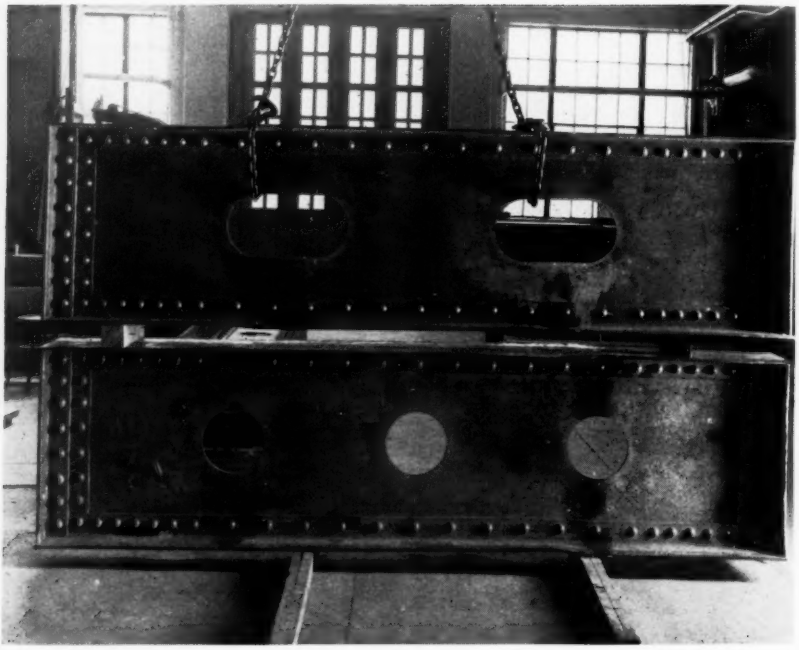

FIGURE 15.—*Columns C6A and C7B after the maximum load test.*

Column *C6A* below Column *C7B*.

2. COLUMNS

(a) MODULUS OF COLUMN AND EFFECTIVE AREA OF PLATE

The moduli, E_s', of hypothetical unperforated plate columns, moduli, E_p', of the tested columns, and effective-area factors, K, with respect to shortening under compressive load, for the plates, are given in table 3.

TABLE 3.—*Moduli of columns, effective-area factors of plates and maximum stress ratios*

Column	*C6A*	*C6B*	*C6* avg.	*C7A*	*C7B*	*C7* avg.
Unperforated-plate column modulus, E_s', kips/in.²	29,600	29,600	29,600	29,700	29,600	29,700
VALUES BASED ON GROSS CROSS-SECTIONAL AREA						
Modulus, E_p', kips/in.²	27,300	26,900	27,100	26,900	26,400	26,600
Effective-area factor, K	0.80	0.76	0.78	0.75	0.71	0.73
Ratio, $\frac{\text{maximum stress}}{P/A}$	−2.58			−2.18		
VALUES BASED ON NET CROSS-SECTIONAL AREA						
Modulus, E_p', kips/in.²	31,200	30,700	31,000	30,700	30,100	30,400
Effective-area factor, K	1.19	1.14	1.16	1.12	1.06	1.09
Ratio, $\frac{\text{maximum stress}}{P/A}$	−2.26			−1.91		

(b) STRESSES

(1) *On the Edge of the Perforation.*—The distribution of stress on the edge of the perforation near midheight of the columns is indicated in figures 3 and 4. The vertical axis of the graph in each figure is a development of one quadrant of the dege of the perforation.

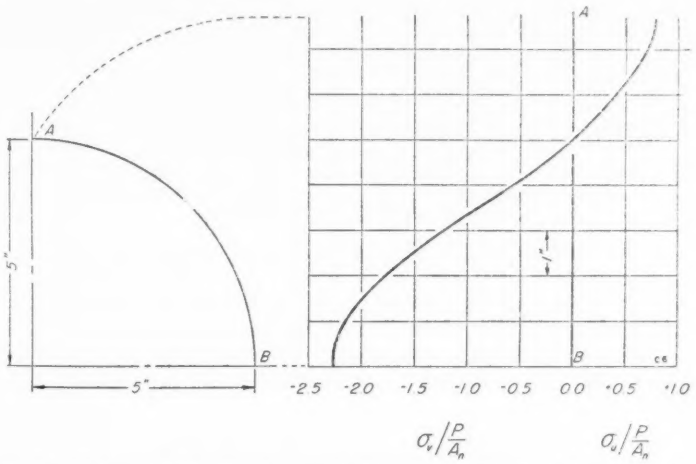

FIGURE 3.—*Column C6A, circular perforation. Distribution of stress on the edge of the middle perforation.*
Based on net area.

In the stress ratios $\sigma_{u,v}/(P/A_n)$, A_n is the net cross-sectional area of the column, and σ_u and σ_v are the maximum and the minimum principal stresses, respectively. The stress ratios based on gross area, $\sigma_{u,v}/(P/A)$, may be obtained by multiplying $\sigma_{u,v}/(P/A_n)$ by 1.14 for either column. The maximum stress ratios are given in table 3.

(2) *On the Surfaces of the Plate.*—The distributions of stress on the surfaces of the plate near midlength of the columns are indicated in figures 5 to 12, inclusive. The stress ratios shown in these figures are based on net area. The stress ratios based on gross area may be obtained by multiplying the given values by 1.14.

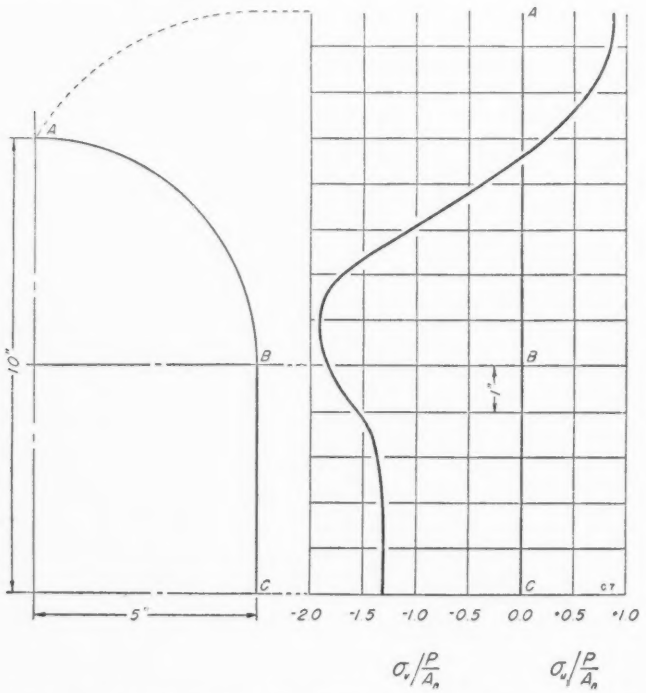

FIGURE 4.—*Column C7A, ovaloid perforation. Distribution of stress on the edge of the perforation near midheight of the column.*

The point *B* is the point of tangency of the circular and straight parts of the edge. Based on net area.

(c) MAXIMUM-LOAD TESTS

(1) *Stress-Strain Graphs.*—The stress-strain graphs for the columns, based on net area, are shown in figure 13. The stresses on gross area may be obtained by multiplying the stresses on net area by 0.88.

(2) *Deflections.*—The stress-lateral-deflection graphs for the columns, based on net area, are shown in figure 14. The stresses on gross area may be obtained by multiplying the stresses on net area by 0.88.

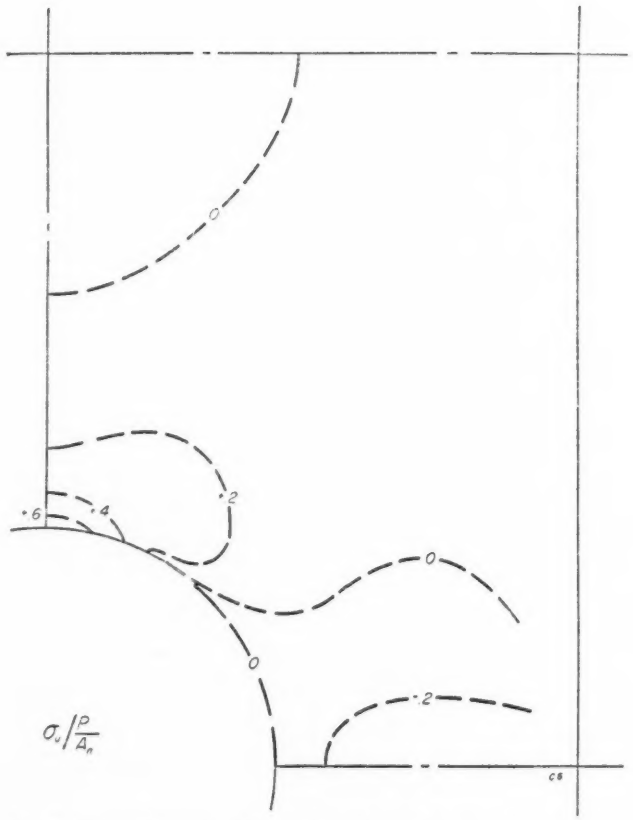

FIGURE 5.—*Column C6A, circular perforation. Isogram of maximum principal stress.*
Based on net area.

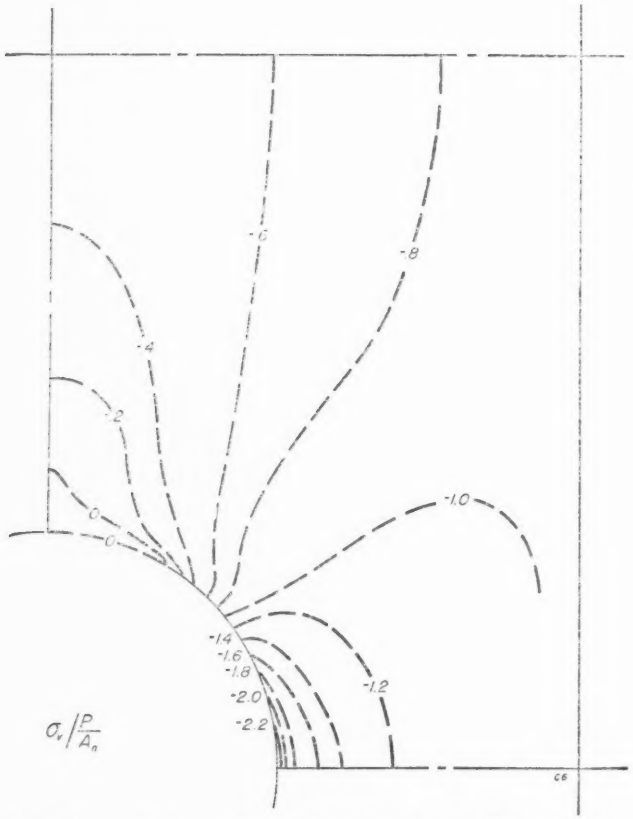

FIGURE 6.—*Column C6A, circular perforation. Isogram of minimum principal stress.*

Based on net area.

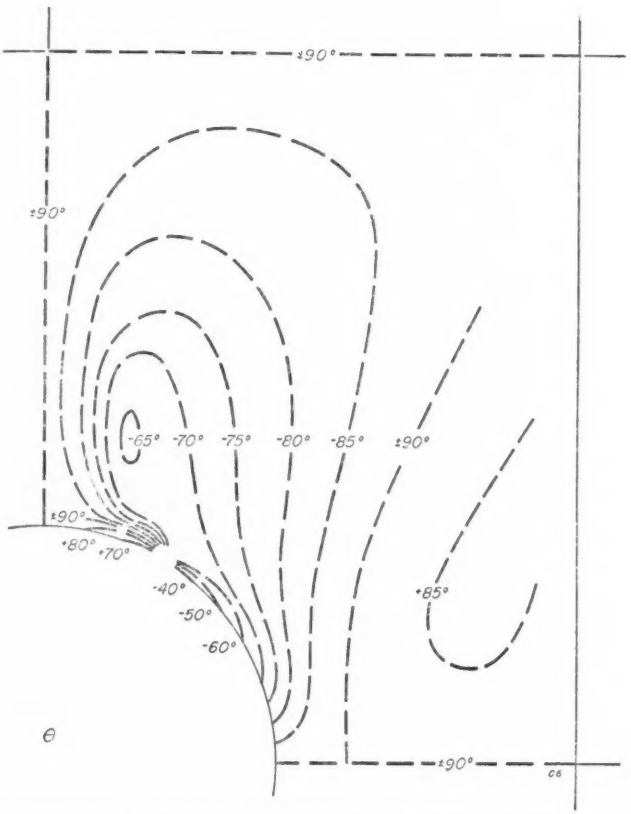

FIGURE 7.—*Column C6A, circular perforation. Isoclinics.*
The angle θ is measured positive counterclockwise from the axis of the column to the direction of the maximum principal stress.

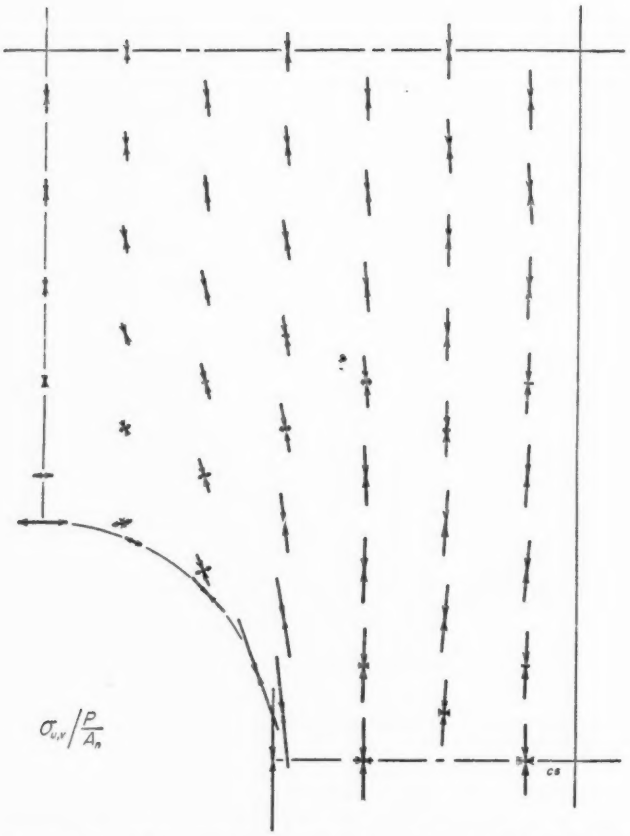

FIGURE 8.—*Column C6A, circular perforation. Magnitude and direction of the principal stresses.*
Based on net area.

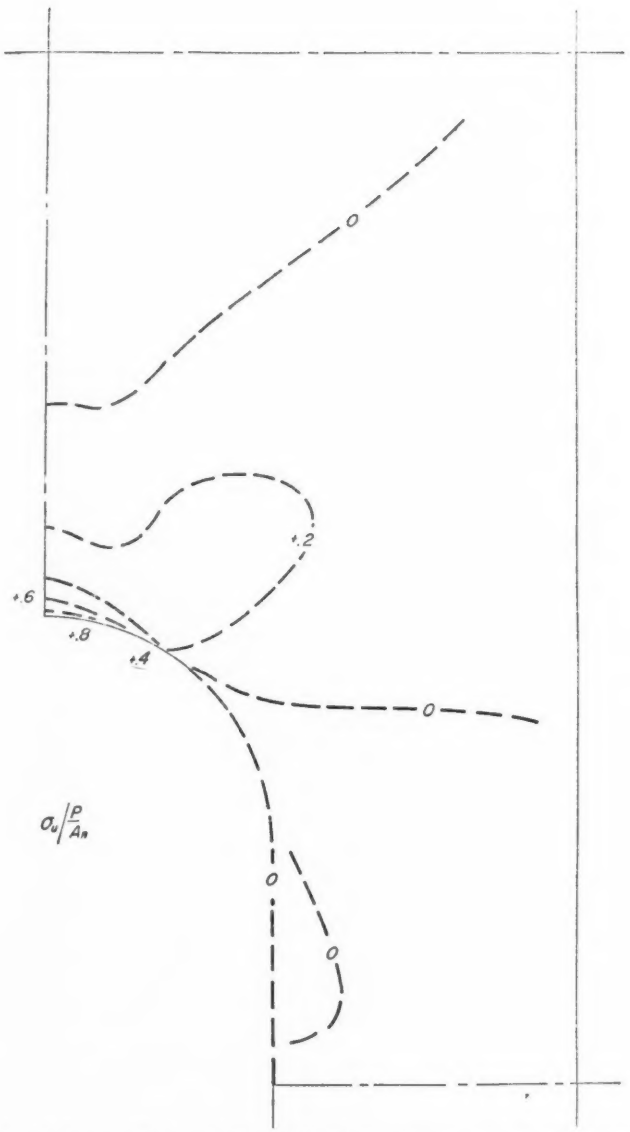

FIGURE 9.—*Column C7A, ovaloid perforation. Isogram of maximum principal stress.*
Based on net area.

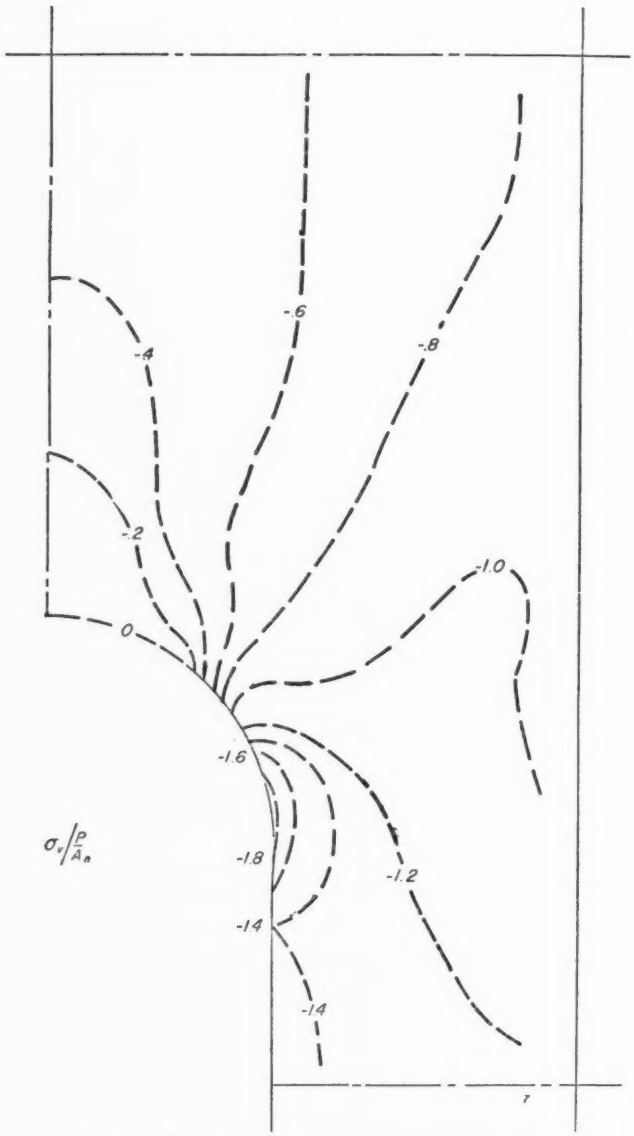

FIGURE 10.—*Column C7A, ovaloid perforation. Isogram of minimum principal stress.*

Based on net area.

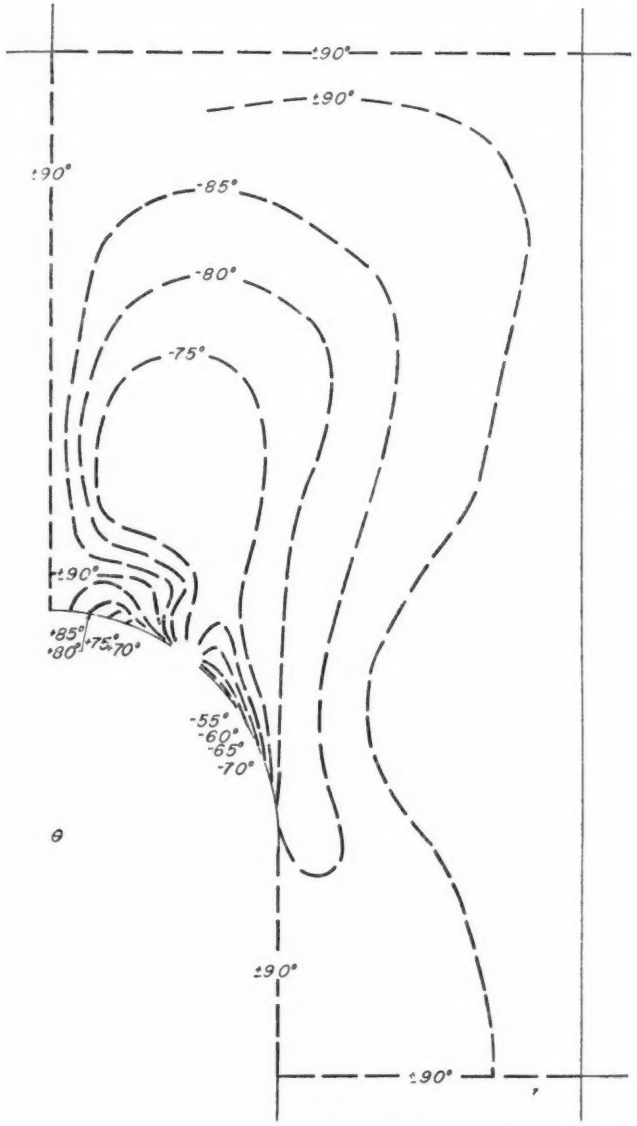

FIGURE 11.—*Column C7A, ovaloid perforation. Isoclinics.*
The angle θ is measured positive counterclockwise from the axis of the column to the direction of the maximum principal stress.

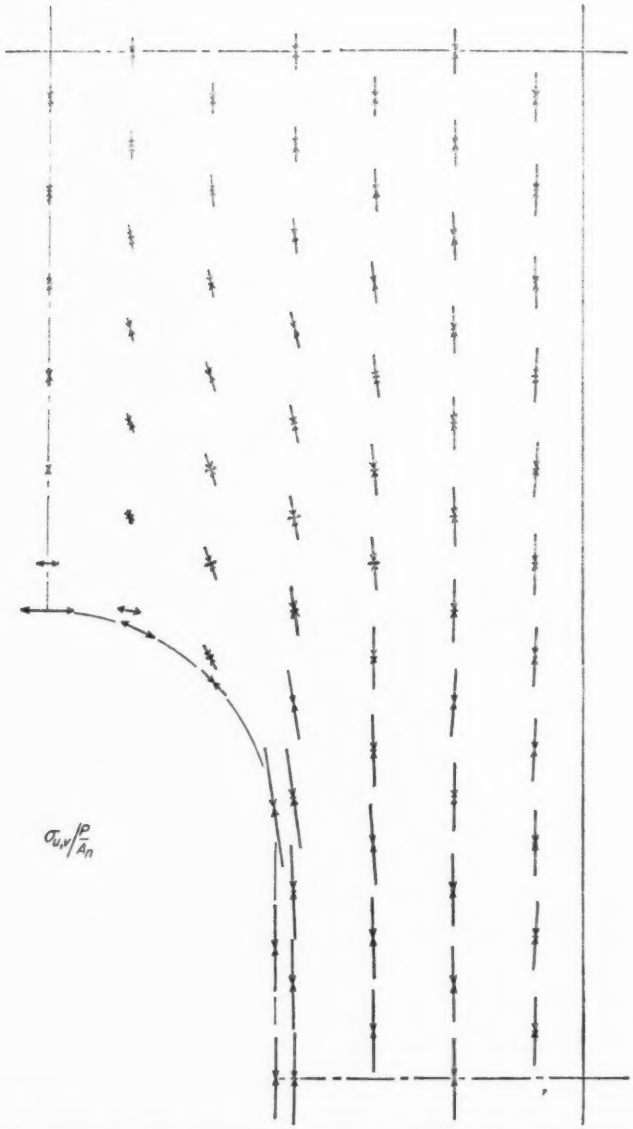

FIGURE 12.—*Column C7A, ovaloid perforation. Magnitude and direction of the principal stresses.*
Based on net area.

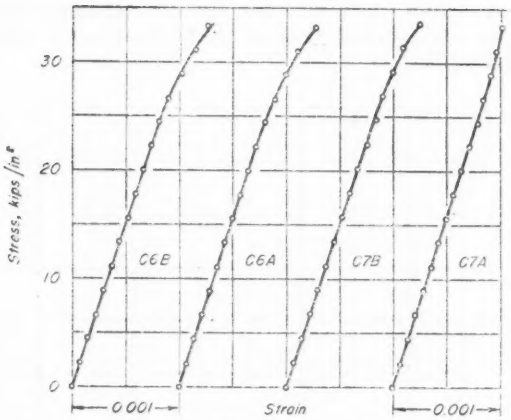

FIGURE 13.—*Columns C6 and C7. Stress-strain graphs.*
Based on net area.

(3) *Maximum Loads.*—The maximum loads for the columns and the maximum average stress on the gross area and on the net area are given in table 4.

TABLE 4.—*Maximum loads for columns*

Column	*C6A*	*C6B*	*C6* avg	*C7A*	*C7B*	*C7* avg
Perforation shape	Circular			Ovaloid		
Perforation spacing, in.	30	30	30	44	44	44
Area of angles, in.²	19.26	19.19	.....	19.18	18.92	.....
Gross area of plate, in.²	11.63	11.63	.....	11.63	11.63	.....
Net area of plate, in.²	7.81	7.78	.....	7.79	7.80	.....
Total gross area, in.²	30.89	30.82	.....	30.81	30.55	.....
Total net area, in.²	27.07	26.97	.....	26.97	26.72	.....
Maximum compressive load, kips	955	1,042	.....	975	932	.....
Compressive stress at failure, kips/in.²:						
On gross area	30.9	33.8	32.4	31.6	30.5	31.1
On net area	35.3	38.6	37.0	36.2	34.9	35.5

The effective-area factors of the plates with respect to compressive stress could not be determined, because no columns with unperforated plates were furnished.

The columns all failed by buckling of the plates near one of the perforations, as may be noted in figure 15. After the maximum load had been reached, secondary buckling occurred in the outstanding legs of the angles near the buckles in the plate.

The average stress at failure for the *C6* columns having circular perforations was somewhat greater than for the *C7* columns having ovaloid perforations.

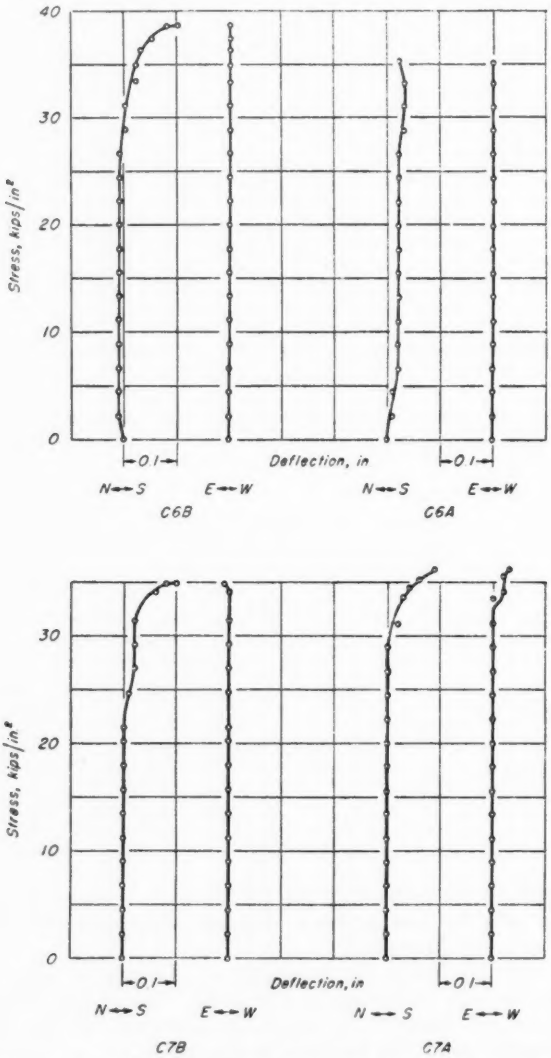

FIGURE 14.—*Columns C6 and C7. Stress-deflection graphs.*
Based on net area.

WASHINGTON, February 6, 1943.

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